# HYDRODEOXYGENATION OF MODEL COMPOUNDS

FINAL REPORT

BY

TECHNICAL DEVELOPMENT DEPARTMENT

SNC INC.

FOR

CANMET, ENERGY, MINES AND RESOURCES, CANADA

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

DSS File No. : 23SQ.23440-0-9178
DSS Contract Serial No. : OSQ81-00118
CANMET Scientific Authority : Dr. E. Furimsky

March 1985
Montreal

108 pp

MICROMEDIA

OCT 11 1985

## ACKNOWLEDGEMENTS

We wish to acknowledge, with thanks, the assistance and contribution of Dr. E. Furimsky, Scientific Authority appointed by CANMET for this project.

Appreciation is also expressed for the contributions made by Dr. H. Baikowitz, President, and Dr. T. Adley, Senior Chemist, Technitrol Canada Ltd.

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## EXECUTIVE SUMMARY

A continuous-flow, high-pressure reactor has been designed and installed at Technitrol Canada Ltd. laboratories, with specifications similar to the one in operation at CANMET laboratories, Ottawa. The hydrodexoygenation of five selected phenols, at a temperature of 350°C with pressures of 1000 and 1500 psi, was investigated in the presence of two commercial catalysts. The five phenols are: phenol, ethylphenol, ortho-methylphenol, 2-6 dimethylphenol and ortho-tertiary butylphenol; the two catalysts were cobalt molybdate in oxidic form and in sulfided form.

The experimental results and correlations were used in a comparative analysis of the hydrodeoxygenation of the phenolic compounds investigated. The percent conversions and the reaction products distribution provided a measure of the reactivity of the phenolic compounds under HDO conditions and the selectivity of the catalyst.

The product distributions were influenced markedly by $H_2$ pressure as well as by the form of the catalyst. In the presence of the sulfided catalyst the relative yields of parent cycloalkane were much higher than those in the presence of the oxidic catalyst.

For the oxide catalyst the decrease in pressure, from 10.34 kPa to 6.89 kPa, resulted in a decrease of the yield of parent aromatic and parent cycloalkane products. This was accompanied by an increase of the yields of products containing no ring substituents or less ring substituents than those of the compound under investigation.

**EXECUTIVE SUMMARY** (Cont'd)

The following reactions for phenol may explain the HDO activity and product distribution obtained in this study:

a) $C_6H_5OH \longrightarrow C_6H_6$

followed by

b) $C_6H_6 \longrightarrow C_6H_{12}$

c) $C_6H_5OH \longrightarrow C_6H_{11}OH \longrightarrow C_6H_{12}$

d) $C_6H_5OH \longrightarrow C_6H_5C_6H_5$

Reaction d) represents a polymerisation of phenol.

The results obtained provide a comparison of the relative HDO activity of the series of selected model compounds.

# 1.0 OBJECTIVES

## 1.0 OBJECTIVES

The main objectives of this study were as follows:

1. To design, assemble and test the installation comprising the continuous-flow, high-pressure reactor, the product receivers, heating system and control panel according to the specifications of the high-pressure system in operation at CANMET laboratories.

2. To investigate the hydrodeoxygenation of selected phenol compounds in the presence of commercial catalysts at predetermined conditions, using the installation erected as in 1. above.

   A. The five phenols selected were as follows:
      (a) phenol
      (b) ethylphenol
      (c) ortho-methylphenol
      (d) 2-6 dimethylphenol
      (e) ortho-tertiary butylphenol

   B. The two catalysts selected were:
      (a) cobalt molybdate - oxidic form
      (b) cobalt molybdate - sulfided form

3. To develop experimental expertize in operation and maintenance of a high pressure bench-scale unit for possible hydrotreatment studies.

# 2.0 INTRODUCTION

## 2.0 INTRODUCTION

Increased interest is now being generated in hydrodeoxygenation (HDO) reactions, particularly because of the need to upgrade synthetic liquids to commercial fuels. Synthetic liquids are derived from coal, oil shale, tar sands and, to a lesser extent, from peat and biomass.

The content of oxygen (O) in such liquids is sometimes an order of magnitude larger than that of S and N. It is generally known that liquids containing large quantities of O-containing compounds are rather unstable, quickly forming deposits on exposure to air (1). Unrefined synthetic liquids are usually of a dark colour with an unpleasant phenolic odour. To maintain stability of commercial fuels derived from synthetic crudes, removal of the reactive O-containing species is necessary. Hydro-refining in the presence of catalysts offers the most proven approach.

It has been shown in the literature that hydrodeoxygenation (HDO) reactions occur simultaneously with hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) during catalytic hydrotreatment of liquid fuels. Extensive research has been done in the areas of HDS and HDN, dictated by environmental concern to limit $SO_2$ and $NO_x$ emissions. HDO has not attracted as much attention, probably due to the very low amounts of oxygen found in conventional crudes (2), the main source of commercial fuels. Also, during HDO, the O is removed in an environmentally harmless form.

The first review on chemistry of HDO was published by Furimsky (3).

## 2.0 INTRODUCTION (Cont'd)

After the issue of this comprehensive summary review, which covered work published until 1983, four other papers have appeared: "Hydroprocessing of Organo-oxygen Compounds in Coal Liquids catalysed by Sulfided Ni-Mo-$\gamma$-$Al_2O_3$" (1984), (4); "Catalytic Hydroprocessing of SRC-II Heavy Distillate Fractions - Hydrodeoxygenation of Phenolic Compounds in the Acidic Fractions" (1985) (5); "Catalytic Hydroprocessing of SRC II Heavy Distillate Fractions - Detailed Structural Characterisation of the Fractions" (1983) (6) and "Hydrodeoxygenation of 1-Napthol Catalyzed by Sulfided Ni-Mo/$\gamma$-$Al_2O_3$: Reaction Network" (1985) (7).

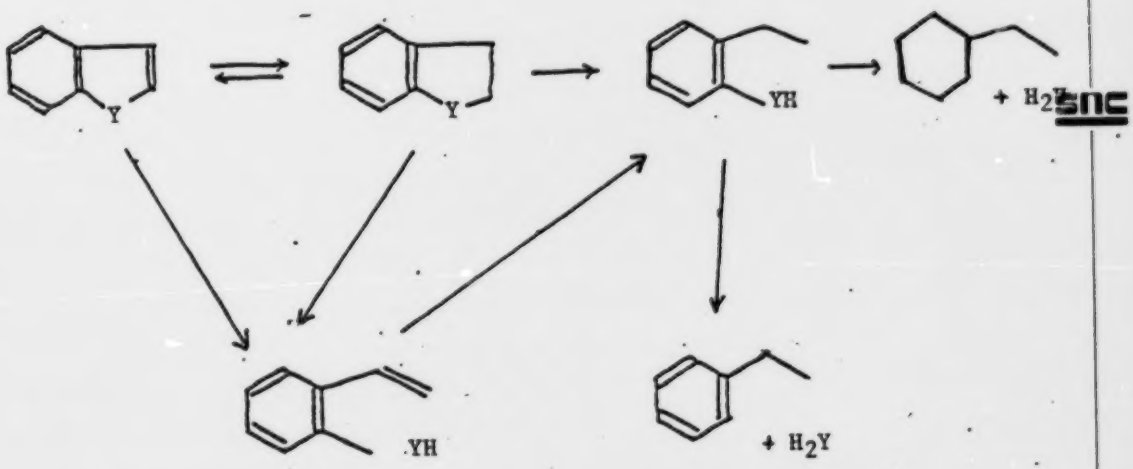
The lack of information on HDO may be attributed to the generally held belief that under the conditions encountered in commercial hydrotreating reactors the removal of oxygen is rapid and complete, relatively little data on the catalytic removal of oxygen is available. Difficulties in analysing small amounts of oxygen in petroleum fractions contributed to this situation as well (2). The HDO of hydrocracked gas oil obtained from Athabasca bitumen using promoted and un-promoted molybdate catalysts was investigated (9) in a bench-scale flow system reactor (10). Neutron activation analysis was utilized to obtain combined oxygen concentration of the order of 1500 ppm.

The relative rates of HDS, HDN and HDO in heavy gas oil have also been investigated. It was observed that the rates of S, N or O removal on supported molybdate catalysts were in qualitative agreement with the relative C-S, C-N and C-O bond strengths (8). Thus, the rate of HDS was shown to be highest followed by HDN and HDO.

## 2.0 INTRODUCTION (Cont'd)

Rollman (11) has also noted that some oxygen containing compounds, O-substituted phenols, are very resistant to hydrogenolysis and complete HDO, probably, does not occur under catalytic hydrotreatment operations.

The possible reaction paths for the hydrogenolysis of heteroring compounds have been proposed by Furimsky (8). As an example, the decomposition of benzofuran in given in Scheme 1.




Y = S,O or NH

**Scheme 1**

It is important to note that ortho substituted phenols are formed through two possible paths: HDO may subsequently occur from the phenol bearing either a saturated or unsaturated side chain (see Scheme 1).

Ortho substituted phenols have been reported to be highly stable and resistant to fixed-bed catalytic hydrotreating (11). It is of particular interest to investigate the ortho substituted phenols in view of their stability as reported by Rollman (11). Such phenols are present in coal derived liquids in high concentrations.

The interest in phenolic compounds with respect to HDO is understandable when one considers that phenolic and furanic structures might account for a substantial portion of O in synthetic crudes. Thus, the increase in total acidity of liquid product from hydrotreatment of heavy gas oil was attributed to conversion of neutral furanic compounds into acidic phenols (2). The presence of phenolic OH was clearly confirmed also in liquids obtained by retorting of oil shale (12).

To establish more accurate stability trends, additional studies on the reactivity of O-containing model compounds, under different conditions, are needed. The present study on phenols is a step in this direction.

For the studies of HDO reactions of phenols and related products the choice of solvents is very critical. Use of common organic solvents would complicate the distribution of products and their quantitative estimation.

Chlorinated solvents such as chloroform or carbon tetrachloride may not be used since acidic species such as HCl will be formed under the conditions of the reaction. Other solvents containing functional groups, e.g. ethers, alcohols, esters and sulfoxides are too restrictive to be used, and may lead to extraneous products arising from reactions such as deposition, esterification, transesterification, etherification, etc.

A solvent is required that would survive HDO reaction conditions intact, and that would not mask the detection and identification of reaction products originating from the compounds under investigation. In this study the n-hexadecane was chosen as the solvent.

It has been shown in previous studies that the presence of an active catalyst is essential for complete elimination of O. Therefore an optimal combination of temperature, concentration and type of reducing agent and an active catalyst must be found to achieve desirable rates of HDO reactions.

The HDO studies of properly selected model compounds may be the base for the elucidation of the overall HDO mechanism. The present study of phenolic model compounds will provide a base for further developments. The selection of phenols is complex because of known differences in reactivities of individual phenols (11).

## 2.0 INTRODUCTION (Cont'd)

In this study, the following compounds were selected for investigation: phenol; ethylphenol; ortho-methylphenol; 2-6 dimethylphenol and ortho-tertiary butylphenol.

It is generally accepted that catalytic reactions take place at the active sites on the catalyst surface and that the catalyst activity is dictated by the concentration of the active sites.

The selection of the catalyst support is also important. This was experimentally demonstrated by Badilla-Ohlbaum et al. in the hydrotreating study of a model feed prepared to simulate liquid products from direct liquefaction of coal (13).

Four catalysts containing the same amount of NiO and $MoO_3$ (4% and 12% respectively) but on different supports showed markedly different HDO activities. The catalyst with the highest surface acidity but the lowest mean pore diameter and pore volume and the smallest surface areas was the catalyst found to be the most active. This effect has been confirmed by other studies as well.

The activity of a catalyst prepared from the three components (support, active ingredient and promoter) depends also on the conditions applied during catalyst preparation. This was demonstrated with four Ni-Mo/$Al_2O_3$ catalysts of the same chemical composition but prepared by different methods (14). These methods altered the order of the impregnating solutions. The effect of different conditions of preparation on HDO activity was quite significant.

Studies on model compounds can provide information on catalyst activity. Further, when sufficient data on the effects of different methods of catalyst preparation and pretreatment are obtained along with detailed product evaluation, the effect of catalyst structure on catalyst activity and selectivity will be determined. Studies of the product distribution from HDO of furan and THF over Co-Mo-$Al_2O_3$ catalyst have been carried out recently (15, 16). It was observed that catalyst pretreatment had a pronounced effect on the HDO of furan. The presulfided form of the catalyst was almost six times more active for HDO of furan than the oxide form. In the case of the THF the product distribution was markedly different and seemed to be affected by the catalyst pretreatment. The present study will provide further data on the effect of catalyst on HDO reactions.

The catalyst used in this study was cobalt molybdate, both in its oxidic and sulfided form. The use of gas chromatograph/mass spectroscopy techniques (GC/MS) for detailed component identification is becoming more prevalent. The approach was used to characterize not only the primary products from coal hydrogenation, but also the liquid obtained after hydrotreatment (17). The components identified were phenol and a series of alkylated monoaromatic phenols. The methyl group was the main substituent in the phenols. In the same liquid, benzofuran (BF) and dibenzofuran (DBF) were found.

Another application of the GC/MS technique was to characterize the product from coal pyrolysis (18). Here again, phenol and

alkylated phenols were detected. The most detailed component identification of coal-derived liquids using this method of GC/MS, (19) identified twenty different phenols plus some other compounds with furanic rings and others with carboxylic groups. The GC/MS technique also identified phenols (mono- and poly-aromatic) and alkylated DBF in a SRC liquid (20).

It may be seen from the above that further investigations of HDO reactions of phenols are needed.

The present study is devoted to catalytic HDO investigation of phenol compounds using a continuous-flow, high pressure reactor designed by SNC and installed at Technitrol Canada Ltd. laboratories. The GC/MS technique has been used for the quantitative evaluation of the reaction products and the conversions during the HDO process.

# 3.0 EXPERIMENTAL INSTALLATION

## 3.0 EXPERIMENTAL INSTALLATION

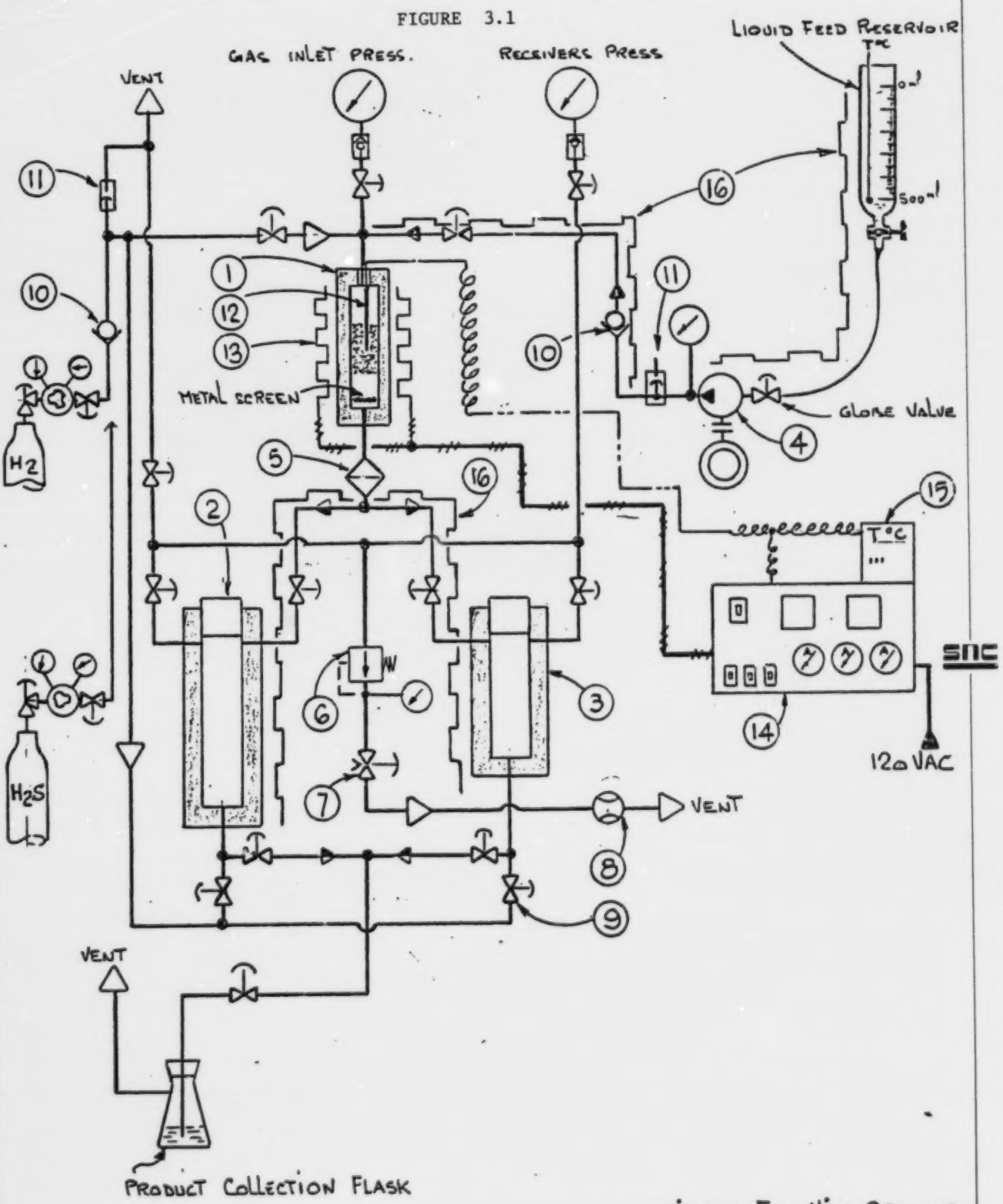
### 3.1 EQUIPMENT

The apparatus used for HDO of the phenolic compounds consisted of a continuous-flow high-pressure reactor and two product-receivers for periodical sample withdrawal (Fig. 3.1). In order to avoid difficulties arising from reactions associated with the start-up or shut-down periods of an experiment (non-steady state), use was made of two receiver vessels. During the start-up period, the products of reaction were collected in one receiver until all the required adjustments had been made to bring the flow rates, temperatures and pressures to the desired levels, i.e. until the system had attained a steady state. As soon as the steady state was attained the flow of products was diverted to the second receiver for the specified sampling period (30 min.). At the end of the sampling period the flow was changed back to the first receiver. By following this procedure the products collected were representative of steady state conditions and free of extraneous effects due to start-up or shut-down.

#### 3.1.1 Reactor

The reactor used in the continuous flow systems was designed by the Technical Development Department of SNC Inc., following the specifications of the reactor used at CANMET. The reactor is a high pressure, double-ended reactor manufactured by A E Autoclave of Canada Ltd., Burlington, Ontario with a capacity of 193ml, 2.5cm internal diameter and length of 38cm. The reactor material

FIGURE 3.1




CONTINUOUS FLOW HIGH PRESSURE REACTION SYSTEM

SCHEMATIC DIAGRAM

3.1.1 **Reactor** (Cont'd)

is stainless steel (SS) -316 and rated at 11 000 psi max. and temperatures up to 427°C. A screen, also of SS-316, was inserted at the bottom of the reactor. The catalyst, either 50 g or 10 g, was supported on a layer of porcelain berl saddles of 10 cm or 15 cm respectively. A pre-heater section of berl saddles was added to within 2 cm of the top of the reactor tube. Sketches of the reactor interior is shown in Figures 3.2 and 3.3. The reactor was tested hydraulically at design pressure. The receivers were made of SS 316, by S H P Enterprises, Montreal, and had an internal diameter of 7.6cm and were rated to 11 000 psi max. The receivers were also heated with the flexible electric heating tape and controlled by the electro-thermal temperature regulator mentioned in Section 3.1.6.

3.1.2 **Temperature Control**

The reactor and the lines leading to the product receivers were electrically heated by an external jacket heater with a variable temperature controller (Elkson Electric C-1271 model, equipped with a three zone proportional regulator).

The temperature of the interior of the reactor was measured by a moveable thermocouple, inserted from above, into a well in the reactor tube; this thermocouple could be moved to obtain the temperatures in the preheater, the catalyst or the support section. The temperature was displayed on a digital Digimite Temperature Indicator manufactured by Thermo Electric of Saddle Brook, N.J.

3.1.3 **High Pressure Flow System**

Hydrogen gas was supplied from commercial cylinders. Hydrogen flow to the head of the reactor was controlled by a pressure reducing regulator valve set to 10 psig (Linde SG 3810-30) and a micrometering valve (A E Autoclave 30 VRMM 4812 GT).

### 3.1.4 Catalysts

The two catalysts used in the investigation were a commercial alumina-supported Cobalt Molybdate Oxidic and its sulfided form (see 4.2.6 ). The commercial Cobalt Molybdate Oxidic catalyst was supplied by Strem Chemicals Inc., Newburyport, Maryland, U.S.A. and had the following specification:

TABLE 3.1

SPECIFICATION OF COMMERCIAL CATALYST

Cobalt Oxide Molybdenum Oxide ($CoO$-$MoO_3$) on alumina
# 27-0480 Lot No 14935-S

| | | | |
|---|---|---|---|
| Form | : | 1/8" x 1/16" extrusions | |
| ABD | : | 37 lbs./cubic ft. | |
| Strength | : | 20 lbs. | |
| SA | : | 175-250 $m^2/g$ | |
| PV | : | .55-.65 cc/g | |
| Typical Analysis | : | $CoO$ | 3-4% (weight per cent) |
| | | $MoO_3$ | 13-15% |
| | | Na | .05% |
| | | $Al_2O_3$ | 80-85% |
| | | Cl | .10% |
| | | S | .10% |
| | | $Fe_2O_3$ | .2% |
| | | Heavy metals | .05% |
| | | $SiO_2$ | .20% |

### 3.1.4 Catalysts (Cont'd)

The catalyst was in the form of cylindrical pellets of .033 - 0.38cm in diameter and lengths varying up to 0.18cm.

### 3.1.5 Reactor Assembly

The reactor was mounted vertically in the flow system so that the feed solutions could be passed from top to bottom (Figure 3.2). In loading the pre-heater and catalyst, the top cap and thermocouple well (Figure 3.3) were tightened into the body of the reactor and the reactor was clamped upside down in the flow system. Measured amounts of porcelain berl saddles and catalyst were poured into the reaction chamber and the pellets settled to the minimum volume. The remaining space was filled with Porcelain berl saddles and the bottom cap and seal rings then tightened into place. The reaction vessel was then ready for connection to the high pressure lines.

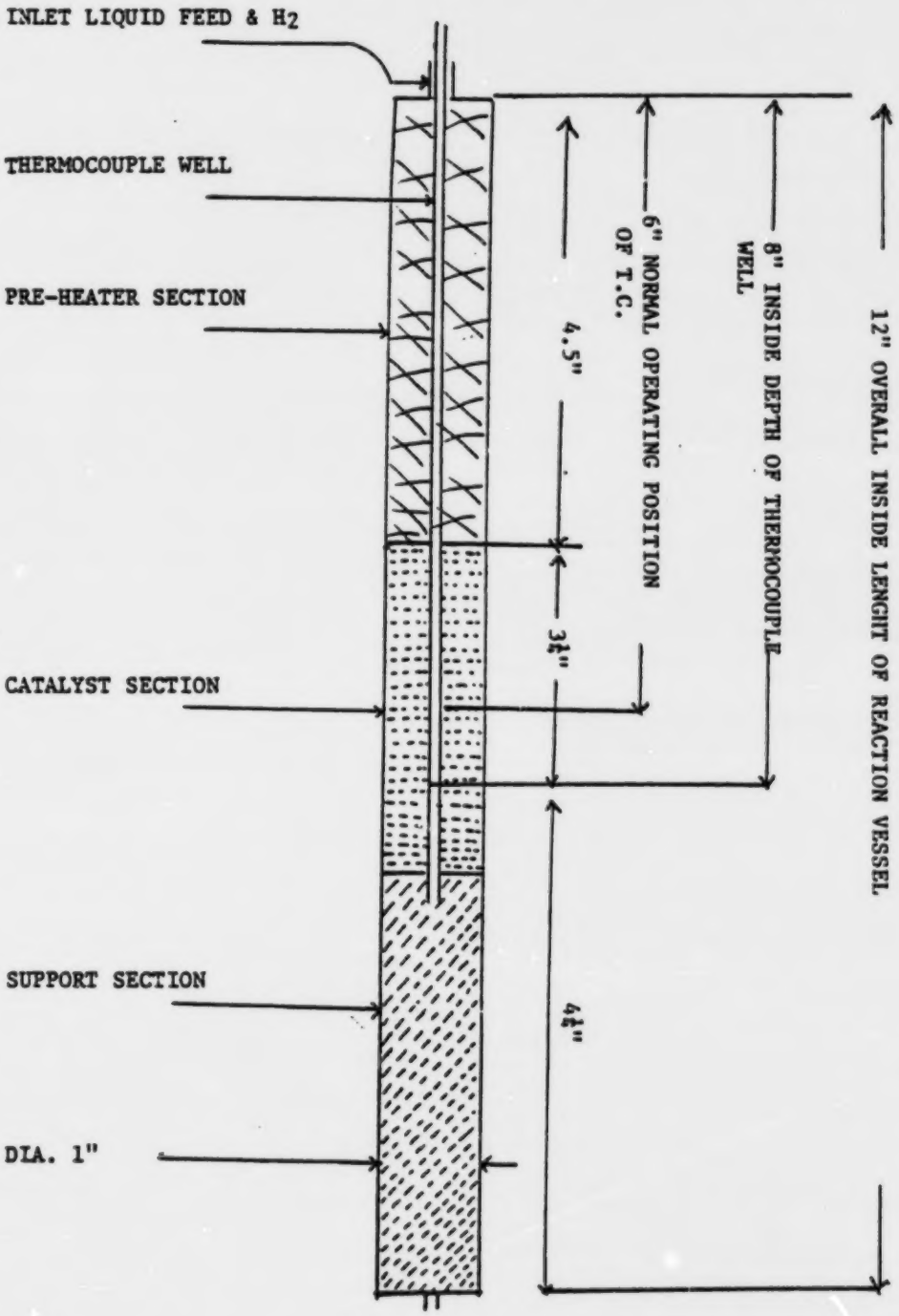



Figure 3.2: The Interior of the Reaction Vessel And the Arrangement of the Pre-Heater And Reaction Bed Sections.

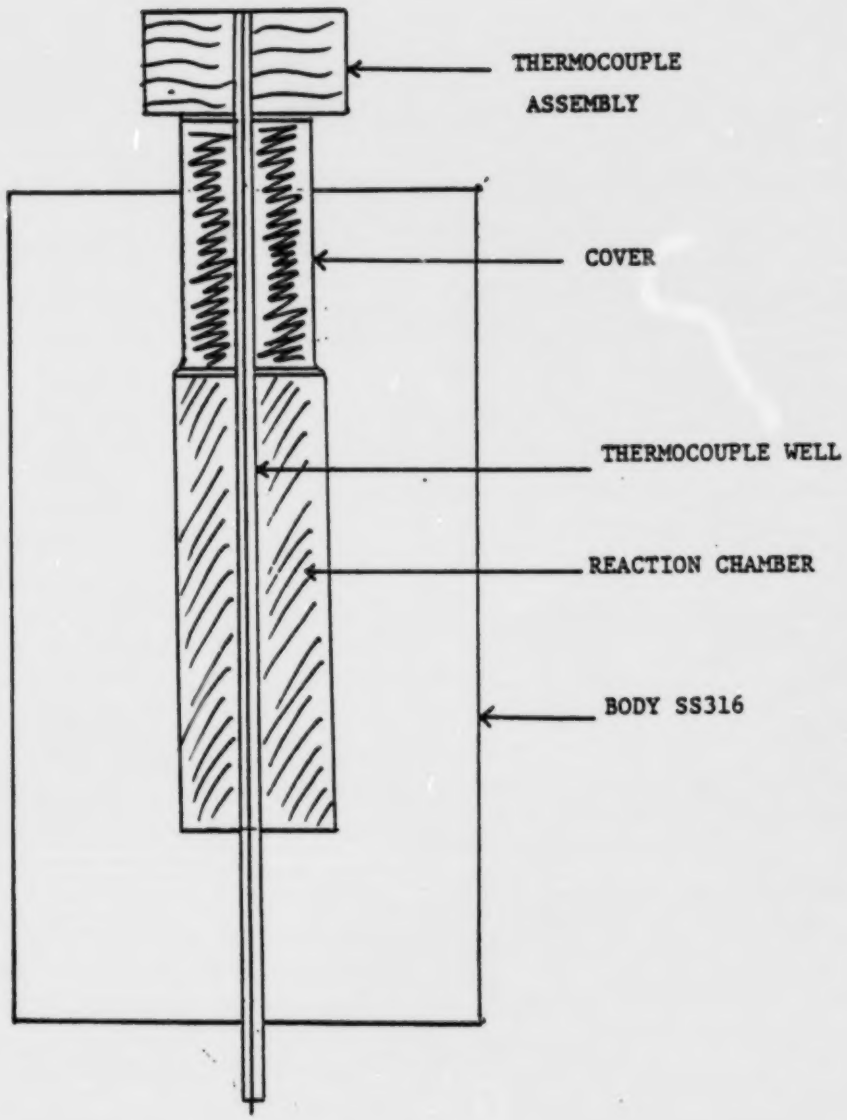



**Figure 3.3: Sketch of the Reaction Vessel**

### 3.1.5 Loading and Pre-treatment (Cont'd.)

The catalyst and pre-heater was used as supplied by the manufacturers. However, in one series of tests, the catalyst was sulfided at the desired reaction temperatures as described in Section 4.2.6 of this report.

### 3.1.6 Liquid Feed System

The liquid feed system consisted of a 500 ml liquid feed reservoir, a globe valve and a diaphragm metering pump. This pump, a Pulsafeeder Products model LS30 with a capacity of 0.15 gpm (0.6 lpm), 20.7 kPa max. W.P., regulated the liquid feed to the reactor. A safety rupture disc assembly, A E Autoclave model CSX 4600 and an A E Autoclave model CXO 4400 stainless steel check valve were placed in the liquid feed line.

The liquid feed reservoir and the lines to the reactor, including the diaphragm metering pump, were heated with 6ft of 1" wide flexible electric heating tape made by Thermolyne Corporation, model 11463-50C, and controlled with a temperature regulator, Electrothermal model MC 221. The liquid feed line from the reservoir was maintained at 60°C to keep the phenols in solution. The liquid feed rate was 0.1 litres/h and the concentration of the phenols varied between 0.88 M and 1.06 M, depending on their solubility and oxygen content.

### 3.1.7 Analysis of Reaction Products

The analysis of the reaction products was carried out on a Perkin Elmer Sigma 5 gas chromatograph equipped with a flame ionization detector and a 5% OV-1 column (85 x 0.32 cm o.d.). Standard heated injectors with glass liners were used.

The initial oven temperature was set at 40°C; the injection port and detector temperature were set at 200°C.

A Finnegan mass spectrometer (GC/MS) equipped with an INCOS data system was used for mass spectrometer analysis. A 3% OV-1 column was used with an initial oven temperature of 40°C.

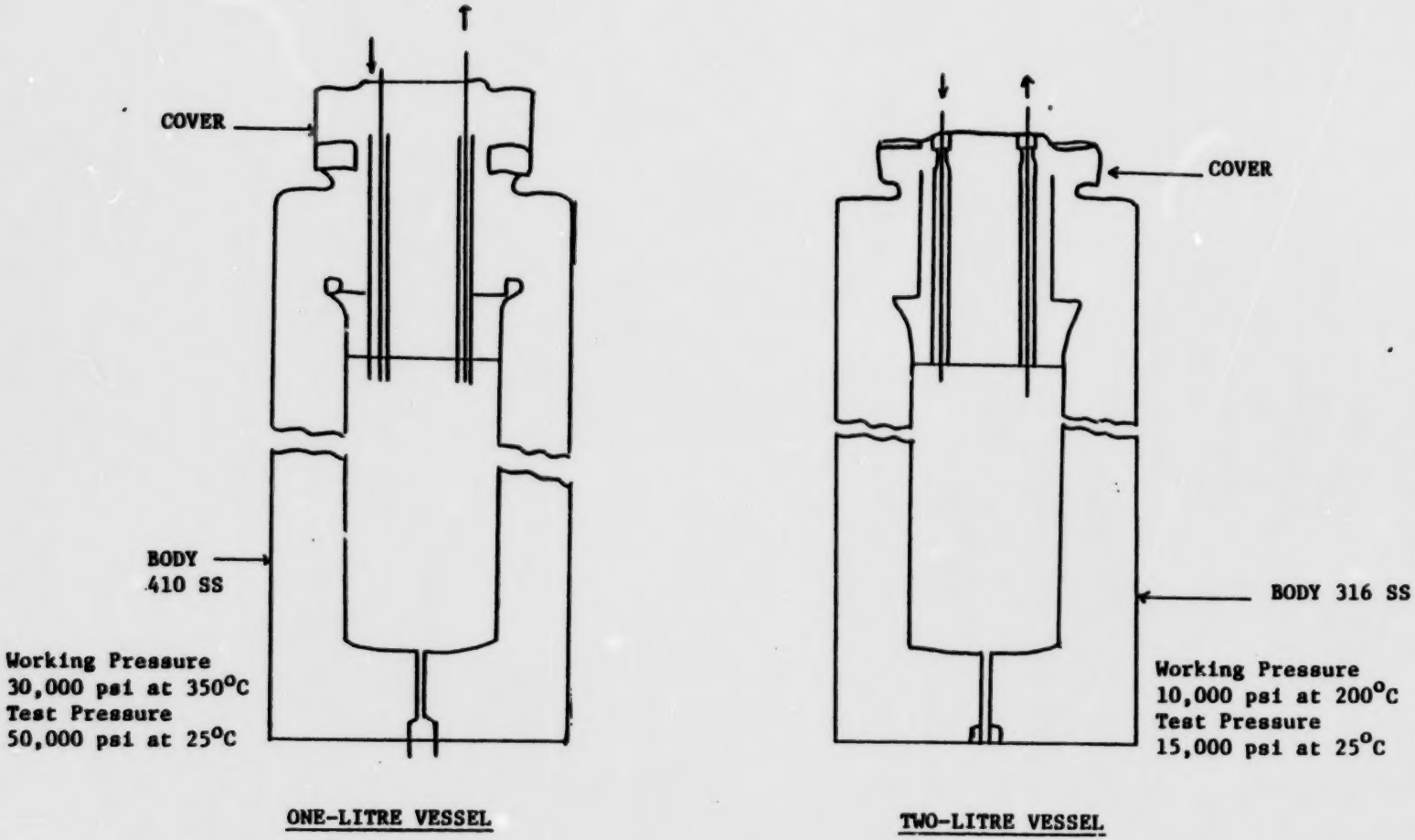



Figure 3.4: The Product Receivers

# 4.0 EXPERIMENTAL PROGRAMME AND PROCEDURE

## 4.0 EXPERIMENTAL PROGRAMME AND PROCEDURE

### 4.1 EXPERIMENTAL PROGRAMME

The experimental programme is summarized in Table 4.1. The programme was established for experiments on HDO of five phenols to be performed in a bench-scale continuous flow, high-pressure reactor system at a temperature of 350°C and two pressures (1500 psi and 1000 psi) using two catalysts: Cobalt Molybdate in oxidic form and Cobalt Molybdate in its sulfided form.

The programme was designed to provide data on the relative rates of HDO of five selected phenols. The results from the experiments could be used to elucidate the effects of substituents at the ortho-positions on HDO of phenols. Finally, the results from this programme would provide further information on the stability of ortho- substituted phenols in fixed-bed catalytic hydrotreating.

The phenols had to be dissolved in a solvent that would remain intact during the experimental conditions applied. The solvent used in this programme was n-Hexadecane. The blank experiments were performed to verify the non-reactive behaviour of the solvent with and without the catalyst at 1500 psi at a temperature of 350°C. These were experiments nos. 1, 2 and 3 shown in Table 4.1 where the bed consisted of Berl Saddles, Cobalt Molybdate Oxidic and Cobalt Molybdate Presulfided respectively.

**TABLE 4.1**

**EXPERIMENTAL PROGRAMME FOR HYDRODEOXYGENATION PROJECT**

| No. | Pre-Heater | Catalyst Bed | Substrate* | Solvent** | No. of Runs | Amount of Catalyst g | Temp. °C | Pressure psi | Comments |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Berl Saddles | Berl Saddles | - | + | 1 | - | 350 | 1500 | Solvent Behaviour |
| 2 | Berl Saddles | Co-Mo-Oxide | - | + | 1 | | 350 | 1500 | Solvent Behaviour |
| 3 | Berl Saddles | Co-Mo-Sulfide | - | + | 1 | | 350 | 1500 | Solvent Behaviour |
| 4 | Berl Saddles | Berl Saddles | + | + | 5 | - | 350 | 1500 | Blank Runs |
| 5 | Berl Saddles | Co-Mo-Oxide | + | + | 5 | 50 | 350 | 1500 | Study Runs |
| 6 | Berl Saddles | Co-Mo-Sulfide | + | + | 5 | 50 | 350 | 1500 | Study Runs |
| 10 | Berl Saddles | Co-Mo-Oxide | + | + | 5 | 50 | 350 | 1000 | Study Runs |
| 11 | Berl Saddles | Co-Mo-Sulfide | + | + | 5 | 50 | 350 | 1000 | Study Runs |
| 15 | Berl Saddles | Co Mo-Sulfide | + | + | 5 | 10 | 350 | 1000 | Study Runs |

* Five model compounds to be tested are: Phenol, 2-Ethylphenol, Orthomethylphenol, 2-6 Dimethylphenol, Ortho-T-Butylphenol

** Hexadecane

4.1 **EXPERIMENTAL PROGRAMME** (Cont'd)

To establish a base line for the reactivity of the solvent, together with the dissolved phenolic compounds, the programme included 5 blank runs (1 run per compound investigated) at 1500 psi and at a temperature of 350°C with the bed of Berl Saddles. These experiments are indicated as type no.4 in Table 4.1.

Experiments type no. 5 of the programme covered the HDO study of the five phenolic compounds at 1500 psi and 350°C with 50g of Cobalt Molybdate Oxidic. Experiments type no. 10 of the programme were similar to type no. 5, except for the pressure (1000 psi rather than 1500 psi).

Experiments type no. 6 of the programme covered the HDO study of the five phenolic compounds at 1500 psi at a temperature of 350°C with 50g of Cobalt Molybdate in presulfided form. Experiments type 11 were similar to type no. 6, except for a pressure of 1000 psi.

Experiments type no. 15 covered the HDO of the five phenolic compounds at 1000 psi at a temparature of 350°C, but with 10g of the catalyst (Cobalt Molybdate in presulfided form) and were to determine the effects of changes in residence time.

The experimental programme included six pre-determined sampling periods over a three-hour duration after the desired operating

4.1 **EXPERIMENTAL PROGRAMME** (Cont'd)

conditions were achieved. All samples were subjected to gas chromatographic analysis. One sample out of the six for every run (either sample 3 or 4) was further subjected to Mass Spectrometer analysis to facilitate the identification and correlation of the reaction products.

## 4.2 EXPERIMENTAL PROCEDURE

A detailed description of the operation of the systems and the steps involved in the collection of the samples is given below.

### 4.2.1 Start-up Period

Prior to start-up, the liquid feed pumps were primed and the reservoir filled with the feed solution to be tested. The catalyst and pre-heater were loaded into the reaction chamber, sulfided where required (see Section 4.2.6) and the vessel connected into the flow system. The reaction vessel and the product receivers were pressurized by opening the inlet valve, allowing hydrogen to flow into the apparatus. Vessels and connections were pressure-tested before proceeding with an experimental run. The system was considered tight if no measurable pressure change (± 10 psi) occurred in a one-hour period. The desired pressure (1500 or 1000 psi) was maintained throughout the duration of the experimental run.

At the beginning of an experiment, all valves except the liquid feed valve were opened to equalize the pressure throughout the system. The flow of hydrogen was started by carefully adjusting the outlet pressure regulator to deliver approximately 10 psig and cautiously opening the metering valve.

### 4.2.2 Sampling

As soon as the steady state was attained the valve connecting the two-litre product receiver to the reactor vessel was closed

4.2.2 **Sampling** (Cont'd)

and the flow directed through the one-litre product receiver. In the meantime the two-litre receiver was emptied and repressurized. After 30 minutes the one-litre receiver was emptied while the product was accumulated in the two-litre receiver. These steps were repeated in 30-minute intervals until the end of experiments.

After specific durations of 0.5 hr., 1.0 hr., 1.5 hrs., 2.0 hrs., 2.5 hrs. and 3.0 hrs. after the start of the experimental runs, samples were withdrawn by cautiously opening the valve in the line connected to the bottom of the product receiver. The gas pressure in the vessel above the liquid forced the product into a pre-weighed Erlenmeyer flask (see Figure 4.1). The amounts of sample were determined by direct weighing and compared with the amounts of feed pumped into the system to establish the weight yields for the conditions of the experiment. The (product receiver) sample vessel was then re-pressurized, either by allowing hydrogen to flow through the reaction vessel or by opening the valve in a by-pass line directly connected to the inlet pressure regulator.

4.2.3 **Presulfidation**

The sulfided form of the catalyst for this investigation was prepared by passing a mixture of $H_2S$ and $H_2$ (1:3) gases through the catalyst bed, maintained at 350°C, at a rate of 50 litres/h for eight hours.

4.2.3 **Presulfidation** (Cont'd)

The outlet opening was connected to a small gas bubbler to provide visual evidence that gas was flowing. The presulfidation continued at 350°C for 45 minutes. The $H_2S$ gas flow was then stopped, the lines quickly removed and the reaction vessel connected to the flow system and pressurized to the desired pressure with hydrogen (1500 or 1000 psi). Depending entirely on the schedule of presulfidation of the experiments, the treated catalyst was either used immediately or allowed to cool slightly overnight in anticipation of a run the following day.

# 5.0 RESULTS AND DISCUSSION

## 5.0 RESULTS AND DISCUSSION

### 5.1 EXPERIMENTAL RESULTS

The samples of the reaction products for each run, designated as samples 1, 2, 3, 4, 5 and 6, i.e. samples taken after 0.5 hr., 1.0 hr., 1.5 hrs., 2.0 hrs., 2.5 hrs. and 3.0 hrs. respectively after the start of the runs were analysed by a Gas Chromatograph. The experimental curves from the Gas Chromatograph are given in Appendix E, Figures E-1 to E-17.

Selected samples of the experimental runs, sample 3 or 4, i.e. samples taken after 1.5 hrs. and 2.0 hrs. after start of the runs, were further analysed by a Mass Spectrometer to determine the percentage composition of the reaction products. These compositions were correlated with the Gas Chromatograph curves for sample 3 or 4 and the peaks of the curves were identified relative to the Mass Spectrometer data. The Mass Spectrometer analyses of the reaction products are presented in Appendix D, Tables D-1 to D-5.

The disposition of the peaks on the Gas Chromatograph curves, identified relative to the components of the reaction products for samples 3 or 4, were further used in correlation of the Gas Chromatograph curves for samples 4 or 3, 1 and 2 of the same runs for which the Mass Spectrometer analyses was done.

The composition of the reaction products for the experimental runs for the five compounds investigated was calculated for samples 1, 2, 3 and 4 and tabulated as follows: samples 3 and 4 in Tables A-1 to A-5 and samples 1 and 2 in Tables A-6 to A-10 in Appendix A. The residence time in terms of the liquid hourly space velocity (LHSV) and the percent conversion were also calculated and tabulated in the tables in Appendix A.

## 5.2 ANALYSES AND DISCUSSION

### 5.2.1 Steady State Reaction

The compositions of the reaction products for samples 3 and 4 of the various runs indicate that steady state for the reaction had been attained when these samples were taken, i.e. 1.5 hrs. and 2.0 hrs. after the start of the reaction. The compositions of the reaction products for samples 1 and 2 of the various runs, i.e. for samples taken 0.5 hr. and 1.0 hr. after the start of the run, indicate lower percentages of the major reaction products than samples 3 and 4. Samples 1 and 2 are therefore considered to be representative of the transient phase. The data in Tables A-1 to A-5 of Appendix A support this analysis.

### 5.2.2 Effect of Hydrogen Pressure

#### 5.2.2.1 Effect of Hydrogen Pressure (Oxidic Catalyst)

The product distribution of HDO experiments performed on the five compounds investigated (average of samples 3 and 4) at 1500 psi and 1000 psi with 50g of catalyst are presented in the following tables 5.1 to 5.4.

**TABLE 5.1**

From Phenol: Runs 50 (1500 psi) and 100 (1000 psi)

| Reaction Products | Runs 50 (1500 psi) | 100 (1000 psi) |
|---|---|---|
| Benzene | 72.2 | 70.0 |
| Toluene | 10.4 | - |
| Dimethylbenzene | 10.7 | 3.6 |
| Cyclohexane | - | 24.5 |
| Dimethylcyclohexane | 6.7 | 1.9 |

5.2.2.1 Effect of Hydrogen Pressure (Oxidic Catalyst) (Cont'd)

**TABLE 5.2**

From 2 Ethylphenol: Runs 51 (1500 psi) and 101 (1000 psi)

| Reaction Products | Runs 51 (1500 psi) | 101 (1000 psi) |
|---|---|---|
| Ethylbenzene | 60.9 | 29.1 |
| Ethylcyclohexane | 32.9 | 18.4 |
| Benzene | 1.3 | 29.9 |
| Cyclohexane | - | 11.7 |
| Dimethylbenzene | 3.2 | - |
| Trimethylcyclohexane | 0.7 | - |
| Toluene | - | 3.8 |
| Tetramethylbenzene | - | 3.5 |
| Methylcyclohexane | - | 3.6 |

**TABLE 5.3**

From Ortho-methylphenol: Runs 52 (1500 psi) and 102 (1000 psi)

| Reaction Products | Runs 52 (1500 psi) | 102 (1000 psi) |
|---|---|---|
| Toluene | 73.1 | 28.7 |
| Methylcyclohexane | 23.9 | 9.8 |
| Dimethylcyclohexane | - | 18.2 |
| Dimethylbenzene | - | 43.4 |

**TABLE 5.4**

From Ortho-Tertiarybutylphenol: Runs 54 (1500 psi) and *104 (1000 psi)

| Reaction Products | Runs 52• (1500 psi) | *104 (1000 psi) |
|---|---|---|
| Benzene | - | 59.4 |
| Cyclohexane | - | 32.0 |
| Dimethylbenzene | - | 6.0 |
| Toluene | - | 2.1 |
| Dimethylcyclohexane | - | 0.6 |

*Data from Mass Spectometer
•Data not available

5.2.2.2 Effect of Hydrogen Pressure (Sulfided Catalyst)

The product distribution of HDO experiments performed on five compounds (average of samples 3 and 4) at 1500 psi and 1000 psi with 50g of catalyst and at 1000 psi with 10g of catalyst are presented in Tables 5.5 to 5.9.

**TABLE 5.5**

From Phenol: Runs 60 (1500 psi) and 110 (1000 psi) with 50g catalyst and
Run 150 (1000 psi) with 10g catalyst

| Reaction Products | Runs 60 (1500 psi) | *1000 (1000 psi) | **150 (1000 psi) |
|---|---|---|---|
| Cyclohexane | 81.9 | 65.0 | 41.7 |
| Benzene | 9.8 | 31.5 | 3.4 |
| Dimethylbenzene | 1.3 | 2.4 | 2.2 |
| Methylcyclohexane | - | - | 24.0 |
| Dimethylcyclohexane | - | 0.8 | 28.3 |
| Trimethylbenzene | 4.2 | 0.8 | - |
| Tetramethylbenzene | 1.0 | - | - |
| Toluene | 1.2 | - | - |

**TABLE 5.6**

From 2 Ethylphenol: Runs 61 (1500 psi) and 111 (1000 psi) with 50g catalyst and
Run 151 (1000 psi) with 10g catalyst

| Reaction Products | Runs 61 (1500 psi) | 111 (1000 psi) | *151 (1000 psi) |
|---|---|---|---|
| Ethylbenzene | 1.9 | 51.7 | 22.8 |
| Ethylcyclohexane | 90.8 | 44.4 | 34.1 |
| Cyclohexane | 3.9 | 0.4 | 27.7 |
| Benzene | - | 0.8 | 6.7 |
| Toluene | - | 1.4 | 2.2 |
| Methylcyclohexane | 3.4 | 1.4 | 6.4 |
| Tetramethylbenzene | - | 0.4 | - |

*Data from Mass Spectrometer
**Data from Sample 3 only

5.2.2.2 Effect of Hydrogen Pressure (Sulfided Catalyst) (Cont'd)

**TABLE 5.7**

From Orthomethylphenol: Run 62 (1500 psi) with 50g catalyst and Run 152(1000 psi) with 10g catalyst

| Reaction Products | *Run 62 (1500 psi) | 152 (1000 psi) |
|---|---|---|
| Methylcyclohexane | 55.2 | 41.9 |
| Cyclohexane | 38.4 | 9.3 |
| Toluene | 3.9 | 44.6 |
| Trimethylbensene | 0.9 | 2.2 |
| Tetramethylbenzene | 0.5 | - |
| Dimethylcyclohexane | 1.1 | 0.5 |
| Benzene | - | 1.0 |
| Dimethylbenzene | - | 0.6 |

**TABLE 5.8**

From 2-6 Dimethylphenol: Runs 63 (1500 psi) and 113 (1000 psi) with 50g of catalyst and Run 153 (1000 psi) with 10g of catalyst

| Reaction Products | Run 63 (1500 psi) | 113 (1000 psi) | 153 (1000 psi) |
|---|---|---|---|
| Dimethylcyclohexane | 39.0 | 32.2 | 12.9 |
| Methylcyclohexane | 18.0 | 15.8 | 5.5 |
| Dimethylbenzene | 20.7 | 35.3 | 71.0 |
| Cyclohexane | 11.3 | 3.9 | 1.3 |
| Toluene | - | 9.7 | 7.9 |
| Tetramethylbenzene | 5.6 | 2.5 | 1.5 |
| Benzene | 4.4 | 0.9 | - |
| Trimethylbenzene | 3.4 | - | 0.7 |

*Data from Mass Spectrometer

5.2.2.2 Effect of Hydrogen Pressure (Sulfided Catalyst) (Cont'd)

**TABLE 5.9**

From Ortho-Tertiarybutylphenol: Run 114 (1000 psi) with 50g of catalyst and
Run 154 (1000 psi) with 10g of catalyst

| Reaction Products | Runs 114 (1000 psi) | 154 (1000 psi) |
|---|---|---|
| Cyclohexane | 78.4 | 77.9 |
| Benzene | 15.7 | 10.o |
| Dimethylcyclohexane | 2.4 | - |
| Dimethylbenzene | 2.0 | 10.5 |
| Toluene | 1.5 | 1.2 |
| Tetramethylbenzene | - | 0.5 |

The effect of the pressure may be discussed in the context of the following tentative reactions which are believed to occur during HDO of phenol.

(a) $C_6H_5OH \longrightarrow C_6H_6$

This is followed to some extent by hydrogenation:

(b) $C_6H_6 \longrightarrow C_6H_{12}$

Depending on the pressure of $H_2$ and the form of catalyst , the ring hydrogenation, followed by dehydration, may occur as well.

(c) $C_6H_5OH \longrightarrow C_6H_{11}OH \longrightarrow C_6H_{12}$

and condensation reactions involving removal of oxygen:

(d) $C_6H_5OH \longrightarrow C_6H_5 \cdot C_6H_5$

The extent to which these reactions take place depends markedly upon the pressure of hydrogen.

Reaction (d) represents a polymerization of phenol. Such reaction is promoted under $H_2$ deficient conditions, and accounts for the formation of coke deposits on catalyst surfaces.

5.2.2. **Effect of Hydrogen Pressure** (Cont'd)

The effect of increase in pressure is really to increase the concentration of hydrogen relative to the feed. This increases the rate of hydrogenation reactions (b) and (c). So, with an increase in pressure of the hydrogen, one should find a greater proportion of Cyclohexane and its derivatives relative to Benzene and its derivatives.

With respect to conversion of phenols, one would expect the conversion of phenols and their derivatives to increase with an increase in pressure. In some of the experiments, e.g. when 50g of catalyst were used there was no significant difference in the conversions at the two pressures. This is attributed to favourable residence times which resulted in almost complete HDO conversion of phenols.

However, with Methylphenol and 2-Ethylphenol, the results follow the explanation of increase in conversion with increase of pressure. In the case of Dimethylphenol, the experiment at one of the pressures (1500 psi) could not be correlated due to probable experimental error.

5.2.3 **Effect of Residence Time**

The effect of the amount of catalyst is reflected in the effect of the change in residence time. Since the diameter of the catalyst bed is the same for all runs, the change in the amount of catalyst results in a change of bed height and therefore the change in residence time for the same flow rates. To assess the effect of residence time, the sulfided cobalt molybdate catalyst was used. Thus, in addition to experiments performed with 50g of catalyst, a series of runs was carried out with 10g of the sulfided

5.2.3 **Effect of Residence Time** (Cont'd)

catalyst at 1000 psi: runs 150, 151, 152, 153 and 154. The comparison of the results from these runs with those from Runs 110, 111, 112, 113 and 114 carried out with 50g of the catalyst at 1000 psi for the five compounds (Tables 5.10 to 5.14) will indicate the effect of residence time on the conversion and the reaction products' distribution.

The products' distribution from HDO of phenols in the presence of 50g and 10g of the sulfided catalyst obtained at 350°C and at $H_2$ pressure of about 1000 psi are compared in the following Tables.

**TABLE 5.10**

| Run | LHSV | Catalyst g | Conv. wt.% | Cyclohexane | Benzene | Methyl Cyclo-hexane | Dimethyl Cyclo-hexane |
|---|---|---|---|---|---|---|---|
| *110 | 0.75 | 50 | 99 | 65.0% | 31.5 | | |
| *150 | 3.45 | 10 | 90 | 41.7% | 3.4 | 24.0 | 28.3 |

*Results are for Sample 3, which correlate with the Mass Spectrometer

**TABLE 5.11**

| Run | LHSV | Catalyst g | Conv. wt.% | Ethyl-benzene | Ethyl Cyclo-hexane | Cyclo-hexane | Benzene |
|---|---|---|---|---|---|---|---|
| 111 | 0.79 | 50 | 99 | 51.7 | 44.4 | 0.4 | 0.8 |
| **151 | 3.77 | 10 | 73 | 34.1 | 22.8 | 27.7 | 6.7 |

**Results from Mass Spectrometer analysis for Sample 3.

5.2.3 Effect of Residence Time (Cont'd)

**TABLE 5.12**

Product Distribution from HDO of 2-Methylphenol

| Run | LHSV | Catalyst g | Conv. wt.% | Methyl Cyclo-hexane | Toluene | Cyclo-hexane |
|---|---|---|---|---|---|---|
| *152 | 4.37 | 10 | 66.3 | 44.6 | 44.6 | 9.3 |
| **62-4 | 0.83 | 50 | 99.0 | 55.2 | 3.9 | 38.4 |

**TABLE 5.13**

Product Distribution from HDO of 2-6 Dimethylphenol

| Run | LHSV | Catalyst g | Conv. wt.% | Dimethyl Cyclo-hexane | Methyl Cyclo-hexane | Dimethyl Benzene | Toluene |
|---|---|---|---|---|---|---|---|
| 113 | 1.08 | 50 | 97.0 | 32.2 | 15.8 | 35.3 | 9.7 |
| 153 | 5.42 | 10 | 81.0 | 12.9 | 5.5 | 71.0 | 7.9 |

**TABLE 5.14**

| Run | LHSV | Catalyst g | Conv. wt.% | Cyclo-hexane | Benzene | Dimethyl-benzene |
|---|---|---|---|---|---|---|
| 114 | 0.92 | 50 | 99.0 | 78.4 | 15.7 | 2.0 |
| 154 | 4.70 | 10 | 90.0 | 77.9 | 10.1 | 10.5 |

The effect of change in the amount of catalyst is really the effect of varying the residence time - expressed as a value for LHSV (Liquid Hourly Space Volume). It is expected that an increase in the LHSV (i.e. a decrease in residence time) would

*Average results of Samples 3 and 4 (1500 psi)
**Data from Mass Spectometer for Sample 4

5.2.3 Effect of Residence Time (Cont'd)

result in a reduction of the time of contact with the catalyst, and would produce a decrease in conversion.

From observations of the Tables 5.10 to 5.14 above, it is seen that the effects of the increase in LHSV (decrease in residence time) are almost the same for all of the phenols investigated, i.e. all phenols exhibited a decrease in conversion with the decrease in residence time, as well as a decrease in the yields of the major components of reactions for the respective phenols.

5.2.4 Effect of Catalyst Presulfidation

The product distribution of HDO experiments performed on five phenolic compounds with oxidic and sulfided molybdate catalyst are compared in the Tables 5.15 to 5.19. The reaction products' compositions are the averages for samples 3 and 4 except where indicated otherwise. Two series of experiments were performed; one at 1500 psi and the other at 1000 psi.

5.2.4 **Effect of Catalyst Presulfidation** (Cont'd)

**TABLE 5.15**

Product distribution of HDO of Phenol at 350°C, 1500 psi and 1000 psi with oxidic and presulfided Molybdate catalyst

| Run | 50 | 60 | 100 | 110 |
|---|---|---|---|---|
| Pressure psi | 1500 | 1500 | 1000 | 1000 |
| Catalyst type | Oxidic | Presulfided | Oxidic | Presulfided |
| Conv. wt.% | 99 | 99 | 99 | 99 |
| **Reaction Products: wt.%** | | | | |
| Benzene | 72.2 | 9.8 | 70.0 | 31.5 |
| Toluene | 10.4 | 1.2 | - | - |
| Dimethylbenzene | 10.7 | 1.3 | 3.6 | 2.4 |
| Cyclohexane | - | 81.9 | 24.5 | 65.0 |
| Dimethylcyclohexane | 6.7 | - | 1.9 | 0.8 |
| Trimethylbenzene | - | 4.2 | - | - |
| Tetramethylbenzene | - | 1.0 | - | - |

**TABLE 5.16**

Product distribution from HDO of 2-Ethylphenol at 350°C, 1500 psi and 1000 psi with oxidic and presulfided Molybdate catalyst

| Run | 51 | 61 | 101 | 111 |
|---|---|---|---|---|
| Pressure psi | 1500 | 1500 | 1000 | 1000 |
| Catalyst type | Oxidic | Presulfided | Oxidic | Presulfided |
| Conv. wt.% | 99 | 97.4 | 88.8 | 99 |
| **Reaction Products: wt.%** | | | | |
| Ethylbenzene | 60.9 | 1.9 | 29.1 | 51.7 |
| Ethylcyclohexane | 32.9 | 90.8 | 18.4 | 44.4 |
| Benzene | 1.3 | - | 29.9 | 0.8 |
| Cyclohexane | - | 3.9 | 11.7 | 0.4 |
| Dimethylbenzene | 3.2 | - | - | - |
| Trimethylcyclohexane | 0.7 | - | - | - |
| Toluene | - | - | 3.8 | 1.4 |
| Tetramethylbenzene | - | - | 3.5 | 0.4 |
| Methylcyclohexane | - | 3.4 | 3.6 | 1.4 |

5.2.4 Effect of Catalyst Presulfidation (Cont'd)

**TABLE 5.17**

Product distribution from HDO of Orthomethylphenol at 350°C, 1500 psi and at 1000 psi with Oxidic and Presulfided Molybdate catalyst

| Run | 52 | 62 | 102 | 112 |
|---|---|---|---|---|
| Pressure psi | 1500 | 1500 | 1000 | 1000 |
| Catalyst type | Oxidic | Presulfided | Oxidic | Presulfided |
| Conv. wt.% | 99 | 99 | 17.6 | 19.5 |
| Reaction products wt.% | | | | * |
| Toluene | 73.1 | 3.9 | 28.7 | - |
| Methylcyclohexane | 23.9 | 55.2 | 9.8 | - |
| Dimethylcyclohexane | - | 1.1 | 18.2 | - |
| Dimethylbenzene | - | - | 43.4 | - |
| Cyclohexane | - | 38.4 | - | - |
| Trimethylbenzene | - | 0.9 | - | - |
| Tetramethylbenzene | - | 0.5 | - | - |
| Benzene | - | - | - | - |

**TABLE 5.18**

Product distribution from HDO of 2-6 Dimethylphenol at 350°C 1500 psi and 1000 psi with Oxidic and Presulfided Molybdate catalyst

| Run | 53 | 63 | 103 | 113 |
|---|---|---|---|---|
| Pressure psi | 1500 | 1500 | 1000 | 1000 |
| Catalyst type | Oxidic | Presulfided | Oxidic | Presulfided |
| Conv. wt.% | 59 | 89.8 | 83.4 | 97.4 |
| Reaction products wt.% | | | | |
| Toluene | 11.7 | - | 16.8 | 9.7 |
| Dimethylbenzene | 67.2 | 20.7 | 36.7 | 35.3 |
| Methylcyclohexane | 12.2 | 18.0 | 11.1 | 15.8 |
| Dimethylcyclohexane | 7.0 | 39.0 | 18.9 | 32.2 |
| Benzene | - | 4.4 | 4.9 | 0.9 |
| Trimethylbenzene | - | 3.4 | 4.3 | - |
| Tetramethylbenzene | - | 5.6 | 4.6 | 2.5 |
| Cyclohexane | - | 11.3 | 2.1 | 3.9 |
| Trimethylcyclohexane | - | - | 0.7 | - |

*Data not available; probable experimental error

5.2.4 Effect of Catalyst Presulfidation (Cont'd)

**TABLE 5.19**

Product distribution from HDO of Ortho-tertiarybutylphenol at 350°C, 1500 psi and 1000 psi with Oxidic and Presulfided Molybdate catalyst

| Run | 54* | 64* | 104** | 114 |
|---|---|---|---|---|
| Pressure psi | 1500 | 1500 | 1000 | 1000 |
| Catalyst type | Oxidic | Presulfided | Oxidic | Presulfided |
| Conv. wt.% | 99 | 97.7 | 99 | 98.8 |
| Reaction Products wt.% | | | | |
| Benzene | | | 59.4 | 15.7 |
| Cyclohexane | | | 32.0 | 78.4 |
| Dimethylbenzene | | | 6.0 | 2.0 |
| Toluene | | | 2.1 | 1.5 |
| Dimethylcyclohexane | | | 0.6 | 2.4 |

*Data on reaction products not available
**Data from Mass Spectrometer

As seen from the results in Tables 5.15 - 5.19, the product distribution is influenced by the catalyst presulfidation. For example, at the same $H_2$ pressure, in the presence of the sulfided catalyst the relative yields of parent cycloalkane were markedly higher than those in the presence of the oxidic catalyst. For the sulfided catalyst, the parent aromat and cycloalkane were the major products. However, during HDO of dimethylphenol, relatively high yields of toluene and methylcyclohexane indicate the presence of dealkylation reactions. The $H_2$ pressure decrease, from 1500 to 1000 psi, resulted in a decrease of the yield of parent cycloalkane due to the increase of the yield of the parent aromatic. At the same time, the sum of parent products, as well as the overall HDO conversion, showed little change except in the case of Orthomethylphenol and this was probably due to steric hindrance, as previously suggested by Rollman (11).

5.2.4 Effect of Catalyst Presulfidation (Cont'd)

The sulfided form of the catalyst appears to favour the hydrocracking of $C_{AR}$–$C_{ALI}$ bond. This is supported by higher yields of products containing the less alkyls in the aromatic ring than the reactant at higher $H_2$ pressures. This is in agreement with the observation made by Penniger (21).

The carbon contents of the spent catalysts (Appendix C) support the argument that presulfidation slows down coke deposition on the catalyst surface.

# 6.0 CONCLUSIONS

## 6.0 CONCLUSIONS

The results obtained in this study provide the product distribution from HDO of five selected phenols, namely: phenol, 2 ethylphenol, orthomethylphenol, 2-6 dimethylphenol and orth-tertiary butyl phenol in the presence of a cobalt molybdate catalyst in its sulfided, as well as oxidic, form. The experiments were performed at 350°C and the pressure at 1500 psi and 1000 psi.

It appears that the ring hydrogenation is not an essential requirement for high HDO conversion of phenols. This translates into a low $H_2$ consumption during hydrotreatment of coal derived liquids. The extent of ring hydrogenation depends on residence time, catalyst pretreatment, $H_2$ pressure and the structure of phenol. The optimal processing conditions may then exist at which the HDO conversions are high whereas the $H_2$ consumption is relatively low. It is, however, known that during hydrotreatment of coal derived liquids, in which phenols are in high concentrations, the $H_2$ consumptions are rather high. This may be attributed to nitrogen bases and polynuclear aromatic compounds which usually accompany phenols in the liquids. These species have a high proton affinity. This means that they can efficiently destroy the Bronstedt acidity on the catalyst surface, thus depleting the concentration of active hydrogen. Moreover, the protonated species are believed to combine to form the precussions and as such they deactivate the catalyst surface. Thus, many factors seem to influence the activity and lifetime of catalysts used for upgrading of synthetic crudes containing high concentrations of phenols.

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## 7.0 REFERENCES


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APPENDICES

## APPENDIX A

SNC

Effect of Catalyst type, Pressure and Residence Time (LHSV) on Hydrodeoxygenation of Phenols (Reaction Temperature 350° C)

TABLE A-1: EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF PHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -3: SAMPLE TAKEN AFTER 1.5 HOURS; DESIGNATION -4: SAMPLE TAKEN AFTER 2.0 HOURS

| Run No | Catalyst | LHSV h-1 | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 40-3 | - | | 1500 | None | | | | | | | | | | | | |
| 40-4 | - | | 1500 | None | | | | | | | | | | | | |
| 50-3 | Co-Mo-O 50 g | 0.55 | 1500 | 99 | - | 73.0 | 10.5 | 10.5 | - | - | - | 6.0 | - | - | - | - |
| 50-4 | Co-Mo-O 50 g | 0.55 | 1500 | 99 | - | 71.4 | 10.3 | 10.9 | - | - | - | 7.4 | - | - | - | - |
| 60-3 | Co-Mo-S 50 g | 0.62 | 1500 | 99 | 81.0 | 9.0 | 2.4 | 1.2 | 5.7 | 0.6 | - | - | - | - | - | - |
| 60-4 | Co-Mo-S 50 g | 0.62 | 1500 | 99 | 82.8 | 10.6 | - | 1.4 | 2.7 | 1.3 | - | - | - | 1.3 | - | - |
| 100-3 | Co-Mo-O 50 g | 0.76 | 1000 | 99 | 34.0 | 57.2 | - | 6.3 | - | - | - | 2.5 | - | - | - | - |
| 100-4 | Co-Mo-O 50 g | 0.76 | 1000 | 99 | 15.1 | 82.8 | - | 0.9 | - | - | - | 1.3 | - | - | - | - |
| 110-3 | Co-Mo-S 50 g | 0.75 | 1000 | 99 | | | | | | | | | | | | |
| 110-4 | Co-Mo-S 50 g | 0.75 | 1000 | 99 | | | | | | | | | | | | |
| 150-3 | Co-Mo-S 50 g | 3.45 | 1000 | 90 | 41.7 | 3.4 | - | 2.6 | - | - | 24.0 | 28.3 | - | - | - | - |
| 150-4 | Co-Mo-S 50 g | 3.45 | 1000 | 90 | 20.6 | 3.4 | - | 1.7 | - | - | 68.3 | 6.1 | - | - | - | - |

TABLE A-2 : EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF 2- ETHYLPHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -3: SAMPLE TAKEN AFTER 1.5 HOURS; DESIGNATION -4: SAMPLE TAKEN AFTER 2.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 41-3 | - | | 1500 | None | | | | | | | | | | | | |
| 41-4 | - | | 1500 | None | | | | | | | | | | | | |
| 51-3 | Co-Mo-O 50 g | 0.69 | 1500 | 99 | - | - | - | 3.5 | - | - | - | - | 1.3 | - | 32.3 | 62.3 |
| 51-4 | Co-Mo-O 50 g | 0.69 | 1500 | 99 | - | 2.6 | - | 2.9 | - | - | - | - | - | - | 33.5 | 59.4 |
| 61-3 | Co-Mo-S 50 g | 0.65 | 1500 | 95 | 3.5 | - | - | - | - | - | 4.3 | - | - | - | 90.1 | 2.1 |
| 61-4 | Co-Mo-S 50 g | 0.65 | 1500 | 98 | 4.3 | - | - | - | - | - | 2.5 | - | - | - | 91.5 | 1.7 |
| 101-3 | Co-Mo-O 50 g | 0.75 | 1000 | 89.1 | 11.7 | 29.9 | 3.8 | - | - | 3.5 | 3.6 | - | - | - | 18.4 | 29.1 |
| 101-4 | Co-Mo-O 50 g | 0.75 | 1000 | 88,5 | - | - | | | | | | | | | | |
| 111-3 | Co-Mo-S 50 g | 0.79 | 1000 | 99 | 0.4 | 0.9 | 1.0 | - | - | 0.4 | 1.4 | - | - | - | 40.9 | 55.2 |
| 111-4 | Co-Mo-S 50 g | 0.79 | 1000 | 99 | 0.5 | 0.7 | 1.7 | - | - | - | 1.4 | - | - | - | 47.8 | 48.1 |
| 151-3 | Co-Mo-S 10 g | 3.77 | 1000 | 65 | 27.7 | 6.7 | 2.2 | - | - | - | 6.4 | - | - | - | 34.1 | 22.8 |
| 151 4 | Co-Mo-S 10 g | 3.77 | 1000 | 75 | 4.8 | 7.2 | 1.5 | - | - | - | 0.6 | - | - | - | 39.8 | 46.2 |

TABLE A-3: EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF METHYL PHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION 3: SAMPLE TAKEN AFTER 1.5 HOURS; DESIGNATION -4: SAMPLE TAKEN AFTER 2.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclohexane | Benzene | Toluene | Dimethyl benzene | Trimethyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 42-3 | - | | 1500 | None | | | | | | | | | | | | |
| 42-4 | - | | 1500 | None | | | | | | | | | | | | |
| 52-3 | Co-Mo-O 50 g | 0.88 | 1500 | 99 | - | - | 70.9 | - | - | - | 27.0 | - | - | - | - | - |
| 52-4 | Co-Mo-O 50 g | 0.88 | 1500 | 95 | - | - | 75.3 | - | - | - | 20.8 | - | - | - | - | - |
| 62-4 | Co-Mo-S 50 g | 0.83 | 1500 | 99 | 38.4 | - | 3.9 | - | 0.9 | 0.5 | 55.2 | 1.1 | - | - | - | - |
| 62-5 | Co-Mo-S 50 g | 0.83 | 1500 | 99 | 2.7 | 2.4 | 6.7 | - | 4.8 | 0.5 | 75.0 | 8.0 | - | - | - | - |
| 102-3 | Co-Mo-O 50 g | 1.02 | 1000 | 18.2 | - | - | 27.0 | 41.1 | - | - | 13.0 | 18.9 | - | - | - | - |
| 102-4 | Co-Mo-O 50 g | 1.02 | 1000 | 13.2 | - | - | 30.4 | 45.7 | - | - | 6.5 | 17.4 | - | - | - | - |
| 112-3 | Co-Mo-S 50 g | 1.02 | 1000 | 24 | | | | | | | | | | | | |
| 112-4 | Co-Mo-S 50 g | 1.02 | 1000 | 15 | | | | | | | | | | | | |
| 152-3 | Co-Mo-S 10 g | 4.37 | 1000 | 60 | 13.2 | 1.2 | 38.4 | 0.8 | 4.2 | - | 41.7 | 0.5 | - | - | - | - |
| 152-4 | Co-Mo-S 10 g | 4.37 | 1000 | 72.5 | 5.3 | 0.8 | 50.8 | 0.4 | 0.1 | - | 42.0 | 0.5 | - | - | - | - |

TABLE A-4: EFFECT OF CATALYST, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF DIMETHYL PHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -3: SAMPLE TAKEN AFTER 1.5 HOURS; DESIGNATION -4: SAMPLE TAKEN AFTER 2.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 43-3 | - | | 1500 | None | | | | | | | | | | | | |
| 43-4 | - | | 1500 | None | | | | | | | | | | | | |
| 53-3 | Co-Mo-O 50 g | 0.98 | 1500 | 50 | - | - | 13.1 | 67.0 | - | - | 12.4 | 7.4 | - | - | - | - |
| 53-4 | Co-Mo-O 50 g | 0.98 | 1500 | 68 | - | - | 10.2 | 67.5 | - | - | 11.9 | 6.5 | - | - | - | 4.0 |
| 63-3 | Co-Mo-S 50 g | 0.92 | 1500 | 87 | 13.9 | 4.4 | - | 22.5 | 5.2 | 9.8 | 12.1 | 32.2 | - | - | - | - |
| 63-4 | Co-Mo-S 50 g | 0.92 | 1500 | 92 | 8.7 | - | - | 18.8 | 1.5 | 1.4 | 28.8 | 45.8 | - | - | - | - |
| 103-3 | Co-Mo-O 50 g | 1.08 | 1000 | 82 | 2.1 | 4.9 | 16.8 | 36.7 | 4.3 | 4.6 | 11.1 | 18.9 | 0.7 | - | - | - |
| 103-4 | Co-Mo-O 50 g | 1.08 | 1000 | 84 | | | | | | | | | | | | |
| 113-3 | Co-Mo-S 50 g | 1.08 | 1000 | 96 | 5.3 | 1.0 | 5.8 | 34.8 | - | 4.4 | 15.8 | 32.9 | - | - | - | - |
| 113-4 | Co-Mo-S 50 g | 1.08 | 1000 | 98 | 2.5 | 0.7 | 13.5 | 35.8 | - | 0.5 | 15.7 | 31.5 | - | - | - | - |
| 153-3 | Co-Mo-S 10 g | 5.42 | 1000 | 97.6 | 0.4 | - | 6.3 | 70.3 | 0.6 | 2.0 | 6.8 | 13.6 | | - | - | - |
| 153-4 | Co-Mo-S 10 g | 5.42 | 1000 | 65 | 1.1 | - | 9.5 | 71.6 | 0.7 | 1.0 | 4.1 | 12.1 | - | - | - | |

TABLE A-5: EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF TERTIARY BUTYL PHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -3 : SAMPLE TAKEN AFTER 1.5 HOURS; DESIGNATION -4 : SAMPLE TAKEN AFTER 2.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 14-3 | | | 1500 | None | | | | | | | | | | | | |
| 14-4 | | | 1500 | None | | | | | | | | | | | | |
| 54-3 | Co-Mo-O 50 g | 0.80 | 1500 | 99 | | | | | | | | | | | | |
| 54-4 | Co-Mo-O 50 g | 0.80 | 1500 | 99 | | | | | | | | | | | | |
| 64-3 | Co-Mo-S 50 g | 0.80 | 1500 | 96.6 | | | | | | | | | | | | |
| 64-4 | Co-Mo-S 50 g | 0.80 | 1500 | 99 | | | | | | | | | | | | |
| 104-3 | Co-Mo-O 50 g | 0.92 | 1000 | 97.7 | 32.0 | 59.4 | 2.1 | 6.0 | - | - | - | 0.6 | - | - | - | - |
| 104-4 | Co-Mo-O 50 g | 0.92 | 1000 | 97.7 | 10.03 | 83.3 | 2.1 | - | - | - | - | 4.4 | - | - | - | - |
| 114-3 | Co-Mo-S 50 g | 0.92 | 1000 | 99 | 77.5 | 14.7 | 2.3 | 3.1 | - | - | - | 2.3 | - | - | - | - |
| 114-4 | Co-Mo-S 50 g | 0.92 | 1000 | 99 | 79.3 | 16.6 | 0.7 | 0.9 | - | - | - | 2.6 | - | - | - | - |
| 154-3 | Co-Mo-S 10 g | 4.70 | 1000 | 95 | 83.5 | 3.9 | 1.0 | 10.7 | - | 1.0 | - | - | - | - | - | - |
| 154-4 | Co-Mo-S 10 g | 4.70 | 1000 | 91 | 72.2 | 16.2 | 1.4 | 10.3 | - | - | - | - | - | - | - | - |

TABLE A-6: EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF PHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -1: SAMPLE TAKEN AFTER 0.5 HOURS; DESIGNATION -2: SAMPLE TAKEN AFTER 1.0 HOURS

| Run No | Catalyst | LHSV h-1 | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 50-1 | Co-Mo-O 50 g | 0.55 | 1500 | | | | | | | | | | | | | |
| 50-2 | Co-Mo-O 50 g | 0.55 | 1500 | | | | | | | | | | | | | |
| 60-1 | Co-Mo-S 50 g | 0.62 | 1500 | | 67.2 | 20.7 | 2.7 | 3.0 | - | 2.8 | | | 5.1 | | | |
| 60-2 | Co-Mo-S 50 g | 0.62 | 1500 | | | | | | | | | | | | | |
| 100-1 | Co-Mo-O 50 g | 0.76 | 1000 | | 0.0 | 96.6 | | 1.8 | | | | 1.5 | | | | |
| 100-2 | Co-Mo-O 50 g | 0.76 | 1000 | | 7.1 | 79.8 | | 19.1 | | | | 1.0 | | | | |
| 110-1 | Co-Mo S 50 g | 0.75 | 1000 | | | | | | | | | | | | | |
| 110-2 | Co-Mo-S 50 g | 0.75 | 1000 | | | | | | | | | | | | | |
| 150-1 | Co-Mo-S 10 g | 3.45 | 1000 | | 50.8 | 1.3 | | 2.6 | | | 2.7 | 42.7 | | | | |
| 150-2 | Co-Mo S 10 g | 3.45 | 1000 | | 70.9 | 3.0 | | 3.9 | | | 6.5 | 15.7 | | | | |

TABLE A-7: EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF 2-ETHYL PHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -1: SAMPLE TAKEN AFTER 0.5 HOURS; DESIGNATION -2: SAMPLE TAKEN AFTER 1.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 51-1 | Co-Mo-O 50 g | 0.69 | 1500 | | | | | | | | | | | | | |
| 51-2 | Co-Mo-O 50 g | 0.69 | 1500 | | | | | | | | | | | | | |
| 61-1 | Co-Mo-S 50 g | 0.65 | 1500 | | | | | | | | | | | | | |
| 61-2 | Co-Mo-S 50 g | 0.65 | 1500 | | | | | | | | | | | | | |
| 101-1 | Co-Mo-O | 0.75 | 1500 | | | | | | | | | | | | | |
| 101-2 | Co-Mo-O | 0.75 | 1500 | | | | | | | | | | | | | |
| 111-1 | Co-Mo-S | 0.79 | 1000 | | | | | | | | | | | | | |
| 111-2 | Co-Mo-S | 0.79 | 1000 | | | | | | | | | | | | | |
| 151-1 | Co-Mo-S | 3.77 | 1000 | | 48.7 | 46.1 | 1.7 | | | | 1.7 | | | | | |
| 151-2 | Co-Mo-S | 3.77 | 1000 | | 24.8 | 6.0 | 1.4 | | | | 1.4 | | | | | |

TABLE A-8: EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENCE TIME (LHSV) ON HYDREODEOXYGENATION OF METHYL PHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -1: SAMPLE TAKEN AFTER 0.5 HOURS; DESIGNATION -2: SAMPLE TAKEN AFTER 1.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 52-1 | Co-Mo-O | 0.88 | 1500 | | | | | | | | | | | | | |
| 52-2 | Co-Mo-O | 0.88 | 1500 | | | | | | | | | | | | | |
| 62-1 | Co-Mo-S | 0.83 | 1500 | | | | | | | | | | | | | |
| 62-2 | Co-Mo-S | 0.83 | 1500 | | | | | | | | | | | | | |
| 102-1 | Co-Mo-O | 1.02 | 1000 | | | | 10.3 | 48.4 | | | 6.5 | 34.8 | | | | |
| 102-2 | Co-Mo-O | 1.02 | 1000 | | | | 18.0 | 50.5 | | | 7.2 | 24.3 | | | | |
| 112-1 | Co-Mo S | 1.02 | 1000 | | | | | | | | | | | | | |
| 112-2 | Co-Mo S | 1.02 | 1000 | | | | | | | | | | | | | |
| 152-1 | Co-Mo-S | 4.37 | 1000 | | 14.4 | 19.6 | 1.3 | 0.5 | 5.8 | | 6.0 | 0.6 | | | | |
| 152-2 | Co-Mo-S | 4.37 | 1000 | | 8.3 | 11.9 | 8.8 | 0.1 | 6.5 | | 21.4 | 0.3 | | | | |

TABLE A-9 : EFFECT OF CATALYST TYPE- PRESSURE AND RESIDENCE TIME (LHSV) ON HYDRODEOXYGENATION OF DIMETHYLPHENOL (REACTION TEMPERATURE 350°C)
DESIGNATION -1: SAMPLE TAKEN AFTER 0.5 HOURS; DESIGNATION -2: SAMPLE TAKEN AFTER 1.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 53-1 | Co-Mo-O 50 g | 0.98 | 1500 | | | | | | | | | | | | | |
| 53-2 | Co-Mo-O 50 g | 0.98 | 1500 | | | | | | | | | | | | | |
| 63-1 | Co-Mo-S | 0.92 | 1500 | | | | | | | | | | | | | |
| 63-2 | Co-Mo-S 50 g | 0.92 | 1500 | | | | | | | | | | | | | |
| 103-1 | Co-Mo-O 50 g | 1.08 | 1000 | | 0.6 | 0.6 | 0.5 | 88.8 | 0.6 | 2.1 | 0.4 | 0.1 | 5.9 | | | |
| 103-2 | Co-Mo-O 50 g | 1.07 | 1000 | | 1.9 | 7.5 | 9.3 | 53.6 | 4.6 | 5.3 | 7.7 | 8.1 | 2.0 | | | |
| 113-1 | Co-Mo-S 50 g | 1.08 | 1000 | | 2.4 | 1.0 | 9.7 | 51.8 | | 1.1 | 11.2 | 22.8 | | | | |
| 113-2 | Co-Mo-S 50 g | 1.08 | 1000 | | 2.4 | 2.6 | 10.1 | 52.9 | | 4.9 | 14.5 | 12.6 | | | | |
| 153-1 | Co-Mo-S 10 g | 5.24 | 1000 | | 14.7 | | 6.0 | 6.7 | 6.9 | 52.7 | - | 13.0 | | | | |
| 153-2 | Co-Mo-S 10 g | 5.24 | 1000 | | 4.4 | | 7.4 | 63.5 | 1.4 | 4.5 | 4.3 | 9.6 | | | | |

TABLE A-10: EFFECT OF CATALYST TYPE, PRESSURE AND RESIDENT TIME (LHSV) ON HYDRODEOXYGENATION OF TERTIARY BUTYL PHENOL (REACTION TEMPERATURE 350°C)

DESIGNATION -1 : SAMPLE TAKEN AFTER 0.5 HOURS; DESIGNATION -2 : SAMPLE TAKEN AFTER 1.0 HOURS

| Run No | Catalyst | LHSV $h^{-1}$ | Press. PSI | % Conversion | PRODUCT - COMPOSITION | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cyclo-hexane | Benzene | Toluene | Dimethyl benzene | Tri-methyl benzene | Tetra methyl benzene | Methyl cyclo hexane | Dimethyl cyclo hexane | Trimethyl cyclo hexane | Tetra methyl cyclo hexane | Ethyl cyclo hexane | Ethyl benzene |
| 54-1 | Co-Mo-O 50 g | 0.80 | 1500 | | | | | | | | | | | | | |
| 54-2 | Co-Mo-O 50 g | 0.80 | 1500 | | | | | | | | | | | | | |
| 64-1 | Co-Mo-S 50 g | 0.80 | 1500 | | | | | | | | | | | | | |
| 64-2 | Co-Mo S 50 g | 0.80 | 1500 | | | | | | | | | | | | | |
| 104-1 | Co-Mo-O 50 g | 0.92 | 1000 | | 12.2 | 77.3 | 4.1 | 1.0 | | | | 1.9 | | | | |
| 104-2 | Co-Mo-O 50 g | 0.92 | 1000 | | 18.2 | 72.0 | 3.2 | 5.4 | | | | 1.2 | | | | |
| 114-1 | Co-Mo-S 50 g | 0.92 | 1000 | | 77.9 | 9.7 | 3.3 | 4.6 | | | | 4.6 | | | | |
| 114-2 | Co-Mo-S 50 g | 0.92 | 1000 | | 75.1 | 1.9 | 1.6 | 19.7 | | | | 1.6 | | | | |
| 154-1 | Co-Mo-S 10 g | 4.70 | 1000 | | - | 87.1 | 2.5 | | | 5.8 | | 4.5 | | | | |
| 154-2 | Co-Mo-S | 4.70 | 1000 | | 30.00 | 41.8 | 2.8 | | | 7.7 | | 17.7 | | | | |

## APPENDIX B

Conversions during HDO of Phenols in the presence of Catalyst Cobalt Molybdate (Oxidic and Presulfided)

TABLE B-1

Conversions during HDO of Phenol in the presence of Oxidic and Sulfided Cobalt Molybdate

| Run No | Catalyst | Press. psi | Compounds | CONVERSIONS (wt.%) SAMPLES (1 - 6) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 |
| 50 | Co-Mo-O 50g | 1500 | Phenol | | | 99.0 | 99.0 | | |
| 60 | Co-Mo-S 50g | 1500 | Phenol | 99.0 | 99.0 | 99.0 | 99.0 | 99.0 | 99.0 |
| 100 | Co-Mo-O 50g | 1000 | Phenol | 99.0 | 99.0 | 99.0 | 99.0 | | |
| 110 | Co-Mo-S 50g | 1000 | Phenol | 99.0 | 99.0 | 99.0 | 99.0 | 99.0 | 99.0 |
| 150 | Co-Mo-S 10g | 1000 | Phenol | 82.3 | 82.1 | 89.5 | 91.3 | 90.1 | 82.1 |

TABLE B-2

Conversions during HDO of 2-Ethylphenol in the presence of Oxidic and Sulfided Cobalt Molybdate

C O N V E R S I O N S (wt.%)

| Run No | Catalyst | Press. psi | Compounds | SAMPLES (1 - 6) 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|
| 51 | Co-Mo-O 50g | 1500 | 2-Ethylphenol | | | 99.0 | 99.0 | | |
| 61 | Co-Mo-S 50g | 1500 | 2-Ethylphenol | 32.2 | 86.0 | 95.5 | 99.3 | 99.3 | 99.3 |
| 101 | Co-Mo-O 50g | 1000 | 2-Ethylphenol | 96.2 | 91.1 | 89.1 | 38.5 | 92.6 | 88.2 |
| 111 | Co-Mo-S 50g | 1000 | 2-Ethylphenol | | | 99.0 | 99.0 | | |
| 151 | Co-Mo-S 10g | 1000 | 2-Ethylphenol | 63.8 | 71.9 | 63.8 | 76.2 | 69.4 | 62.9 |

TABLE B-3

Conversions during HDO of Orthomethylphenol in the presence of Oxidic and Sulfided Cobalt Molybdate

| Run No | Catalyst | Press. psi | Compounds | CONVERSIONS (wt.%) SAMPLES (1 - 6) 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|
| 52 | Co-Mo-O 50g | 1500 | Orthomethylphenol | | | 99.0 | 95.0 | | |
| 62 | Co-Mo-S 50g | 1500 | Orthomethylphenol | 66.8 | 71.5 | 99.0 | 99.0 | 99.0 | |
| 102 | Co-Mo-O 50g | 1000 | Orthomethylphenol | 31.4 | 25.5 | 15.9 | 19.3 | 20.1 | 18.0 |
| 112 | Co-Mo-S 50g | 1000 | Orthomethylphenol | 82.7<br>63.3 | 91.1 | 27.9 | - | | |
| 152 | Co-Mo-S 10g | 1000 | Orthomethylphenol | 27.4 | 60.1 | 83.3 | 66.7 | 78.0 | 78.5 |

TABLE B-4

Conversions during HDO of 2-6 Dimethylphenol in the presence of Oxidic and Sulfided Cobalt Molybdate

CONVERSIONS (wt.%)

| Run No | Catalyst | Press. psi | Compounds | SAMPLES (1 - 6) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 |
| 53 | Co-Mo-O 50g | 1500 | 2-6 Dimethylphenol | | | 50.0 | 68.0 | | |
| 63 | Co-Mo-S 50g | 1500 | 2-6 Dimethylphenol | 23.5 | 92.9 | 87.4 | 92.1 | 36.5 | 96.3 |
| 103 | Co-Mo-O 50g | 1000 | 2-6 Dimethylphenol | 20.2 | 67.6 | 82.2 | 84.4 | 86.7 | 38.1 |
| 113 | Co-Mo-S 50g | 1000 | 2-6 Dimethylphenol | 95.6 | 93.3 | 96.6 | 98.2 | 99.0 | 99.0 |
| 153 | Co-Mo-S 10g | 1000 | 2-6 Dimethylphenol | 51.3 | 69.4 | 76.2 | 65.9 | 72.5 | 75.7 |

TABLE B-5

**Conversions during HDO of Ortho-tertiarybutylphenol in the presence of Oxidic and Sulfided Cobalt Molybdate**

| Run No | Catalyst | Press. psi | Compounds | CONVERSIONS (wt.%) SAMPLES (1 - 6) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 |
| 54 | Co-Mo-O 50g | 1500 | Ortho-tertiarybutylphenol | | | 99.0 | 99.0 | | |
| 64 | Co-Mo-S 50g | 1500 | Ortho-tertiarybutylphenol | 95.5 | 96.5 | 99.0 | 99.0 | 99.0 | 99.0 |
| 104 | Co-Mo-O 50g | 1000 | Ortho-tertiarybutylphenol | 95.5 | 95.2 | 97.7 | 97.7 | 97.5 | 96.1 |
| 114 | Co-Mo-S 50g | 1000 | Ortho-tertiarybutylphenol | 98.2 | 98.1 | 98.6 | 98.9 | 98.1 | 99.4 |
| 154 | Co-Mo-S 10g | 1000 | Ortho-tertiarybutylphenol | 28.9 | 76.3 | 91.9 | 38.4 | 95.2 | 94.2 |

## APPENDIX C

Carbon Content of Catalysts after HDO of the Phenolic Compounds Investigated

## TABLE C-1

### CARBON CONTENT OF CATALYST AFTER RUNS
(3 hours of operation)

| Run No. | Investigated | Pressure p s i | Catalyst | Carbon Content wt.% |
|---|---|---|---|---|
| 50 | Phenol | 1500 | Co-Mo-O (50g) | 3.0 |
| 50A | " | 1500 | Co-Mo-O (50g) | 3.5 |
| 60 | " | 1500 | Co-Mo-S (50g) | 2.8 |
| 100 | " | 1000 | Co-Mo-O (50g) | 3.7 |
| 110 | " | 1000 | Co-Mo-S (50g) | 2.9 |
| 150 | " | 1000 | Co-Mo-S (10g) | 3.7 |
| 51 | 2-Ethylphenol | 1500 | Co-Mo-O (50g) | 4.0 |
| 61 | " | 1500 | Co-Mo-S (50g) | 2.7 |
| 101 | " | 1000 | Co-Mo-O (50g) | 3.5 |
| 111 | " | 1000 | Co-Mo-S (50g) | 2.7 |
| 151 | " | 1000 | Co-Mo-S (10g) | 3.1 |
| 52 | Methylphenol | 1500 | Co-Mo-O (50g) | 6.5 |
| 52A | " | 1500 | Co-Mo-O (50g) | 4.4 |
| 62 | " | 1500 | Co-Mo-S (50g) | 2.4 |
| 102 | " | 1000 | Co-Mo-O (50g) | 5.8 |
| 112 | " | 1000 | Co-Mo-S (50g) | 3.3 |
| 152 | " | 1000 | Co-Mo-S (10g) | 3.1 |
| 53 | Dimethylphenol | 1500 | Co-Mo-O (50g) | 3.4 |
| 63 | " | 1500 | Co-Mo-S (50g) | 2.8 |
| 103 | " | 1000 | Co-Mo-O (50g) | 3.9 |
| 113 | " | 1000 | Co-Mo-S (50g) | 3.1 |
| 153 | " | 1000 | Co-Mo-S (10g) | 3.7 |
| 54 | Tertiarybutylphenol | 1500 | Co-Mo-O (50g) | 3.6 |
| 64 | " | 1500 | Co-Mo-S (50g) | 3.3 |
| 104 | " | 1000 | Co-Mo-O (50g) | 3.3 |
| 114 | " | 1000 | Co-Mo-S (50g) | 3.2 |
| 154 | " | 1000 | Co-Mo-S (10g) | 3.1 |
| 20 | - | 1500 | Co-Mo-O (50g) | 3.4 |
| 30 | - | 1500 | Co-Mo-S (50g) | 2.8 |
| 40 | Phenol | 1500 | - | - |
| 42 | Methylphenol | 1500 | - | - |
| 43 | Dimethylphenol | 1500 | - | - |

SNC

## APPENDIX D

Mass Spectrometer Analysis of Reaction Products from HDO of Phenolic Compounds Investigated

TABLE D-1

Mass Spectrometer Analysis of Reaction Products from HDO of Phenol

| Run | Sample | Catalyst | Pressure psi | Reaction Products | Mass Spectrometer Counts | wt.% |
|---|---|---|---|---|---|---|
| 60 | 4 | Co-Mo-S (50g) | 1500 | Cyclohexane | 84 400 | 82.8 |
| | | | | Benzene | 10 800 | 10.6 |
| | | | | Trimethylbenzene | 2 700 | 2.6 |
| | | | | Dimethylbenzene | 1 400 | 1.4 |
| | | | | Tetramethylcyclohexane | 1 300 | 1.3 |
| 100 | 3 | Co-Mo-O (50g) | 1000 | Benzene | 41 000 | 57.2 |
| | | | | Cyclohexane | 24 400 | 34.0 |
| | | | | Dimethylbenzene | 4 500 | 6.3 |
| | | | | Dimethylcyclohexane | 1 800 | 2.5 |
| 110 | | Co-Mo-S (50g) | 1000 | Cyclohexane | 83 000 | 65.0 |
| | | | | Benzene | 40 000 | 31.5 |
| | | | | Dimethylbenzene | 3 900 | 2.4 |
| | | | | Dimethylcyclohexane | 1 000 | 0.8 |
| 150 | 3 | Co-Mo-S (10g) | 1000 | Cyclohexane | 8 800 | 53.3 |
| | | | | Dimethylcyclohexane | 5 000 | 30.3 |
| | | | | Methylcyclohexane | 1 500 | 9.2 |
| | | | | Dimethylbenzene | 600 | 3.6 |
| | | | | Benzene | 600 | 3.6 |

TABLE D-2

Mass Spectrometer Analysis of Reaction Products from HDO of 2-Ethylphenol

| Run | Sample | Catalyst | Pressure psi | Reaction Products | Mass Spectrometer Counts | wt.% |
|---|---|---|---|---|---|---|
| 61 | 4 | Co-Mo-S (50g) | 1500 | Ethylcyclohexane | 23 800 | 65.0 |
| | | | | Cyclohexane | 5 400 | 14.8 |
| | | | | Methylcyclohexane | 4 300 | 11.8 |
| | | | | Ethylbenzene | 3 100 | 8.5 |
| 101 | 3 | Co-Mo-O (50g) | 1000 | Benzene | 29 700 | 29.9 |
| | | | | Ethylbenzene | 28 900 | 29.1 |
| | | | | Ethylcyclohexane | 18 300 | 18.4 |
| | | | | Cyclohexane | 11 600 | 11.7 |
| | | | | Methylbenzene | 3 800 | 3.8 |
| | | | | Methylcyclohexane | 3 600 | 3.6 |
| | | | | Tetramethylbenzene | 3 500 | 3.5 |
| 111 | 3 | Co-Mo-S (50g) | 1000 | Ethylbenzene | 44 200 | 44.0 |
| | | | | Ethylcyclohexane | 33 700 | 33.6 |
| | | | | Methylcyclohexane | 7 100 | 7.1 |
| | | | | Methylbenzene | 4 600 | 4.6 |
| | | | | Benzene | 4 000 | 4.0 |
| | | | | Cyclohexane | 3 900 | 3.9 |
| | | | | Tetramethylbenzene | 2 900 | 2.9 |
| 151 | 3 | Co-Mo-S (10g) | 1000 | Ethylcyclohexane | 22 800 | 34.1 |
| | | | | Cyclohexane | 18 500 | 27.7 |
| | | | | Ethylbenzene | 15 300 | 22.9 |
| | | | | Benzene | 4 500 | 6.7 |
| | | | | Methylcyclohexane | 4 300 | 6.4 |
| | | | | Toluene | 1 500 | 2.2 |

TABLE D-3

Mass Spectrometer Analysis of Reaction Products from HDO of Ortho-Methylphenol

| Run | Sample | Catalyst | Pressure psi | Reaction Products | Mass Spectrometer Counts | wt.% |
|---|---|---|---|---|---|---|
| 62 | 4 | Co-Mo-S (50g) | 1500 | Methylcyclohexane | 113 900 | 55.2 |
| | | | | Cyclohexane | 79 200 | 38.4 |
| | | | | Toluene | 8 000 | 3.9 |
| | | | | Dimethylcyclohexane | 2 300 | 1.1 |
| | | | | Trimethylbenzene | 1 800 | 0.9 |
| | | | | Tetramethylbenzene | 1 000 | 0.5 |
| 102 | 3 | Co-Mo-O (50g) | 1000 | Dimethylbenzene | 7 600 | 41.1 |
| | | | | Toluene | 5 000 | 27.0 |
| | | | | Dimethylcyclohexane | 3 500 | 18.9 |
| | | | | Methylcyclohexane | 2 400 | 13.0 |
| 152 | 3 | Co-Mo-S (10g) | 1000 | Methylcyclohexane | 27 600 | 33.6 |
| | | | | Cyclohexane | 22 100 | 26.9 |
| | | | | Toluene | 20 800 | 25.3 |
| | | | | Benzene | 6 100 | 7.4 |
| | | | | Trimethylbenzene | 2 500 | 3.0 |
| | | | | Dimethylbenzene | 2 100 | 2.6 |
| | | | | Dimethylcyclohexane | 1 000 | 1.2 |

TABLE D-4

Mass Spectrometer Analysis of Reaction Products from HDO of 2-6 Dimethylphenol

| Run | Sample | Catalyst | Pressure psi | Reaction Products | Mass Spectrometer Counts | wt.% |
|---|---|---|---|---|---|---|
| 64 | 4 | Co-Mo-S (50g) | 1500 | Dimethylctclohexane | 32 700 | 45.8 |
| | | | | Methylcyclohexane | 17 000 | 23.8 |
| | | | | Dimethylbenzene | 13 400 | 18.8 |
| | | | | Cyclohexane | 6 200 | 8.7 |
| | | | | Trimethylbenzene | 1 100 | 1.5 |
| | | | | Tetramethylbenzene | 1 000 | 1.4 |
| 103 | 3 | Co-Mo-O (50g) | 1000 | Dimethylbenzene | 81 200 | 36.7 |
| | | | | Dimethylcyclohexane | 41 900 | 18.9 |
| | | | | Toluene | 37 200 | 16.8 |
| | | | | Methylcyclohexane | 24 500 | 11.1 |
| | | | | Benzene | 10 900 | 4.9 |
| | | | | Tetramethylbenzene | 10 200 | 4.6 |
| | | | | Trimethylbenzene | 9 500 | 4.3 |
| | | | | Cyclohexane | 4 600 | 2.1 |
| | | | | Trimethylcyclohexane | 1 500 | 0.7 |
| 113 | 3 | Co-Mo-S (50g) | 1000 | Dimethylbenzene | 13 800 | 34.8 |
| | | | | Dimethylcyclohexane | 41 400 | 32.9 |
| | | | | Methylcyclohexane | 19 900 | 15.8 |
| | | | | Toluene | 7 300 | 5.8 |
| | | | | Cyclohexane | 6 700 | 5.3 |
| | | | | Tetramethylbenzene | 5 500 | 4.4 |
| | | | | Benzene | 1 200 | 1.0 |
| 153 | 3 | Co-Mo-S (10g) | 1000 | Dimethylbenzene | 31 200 | 43.5 |
| | | | | Dimethylcyclohexane | 18 700 | 26.0 |
| | | | | Methylcyclohexane | 9 200 | 12.8 |
| | | | | Toluene | 5 900 | 8.2 |
| | | | | Tetramethylbenzene | 3 800 | 5.3 |
| | | | | Trimethylbenzene | 1 900 | 2.6 |
| | | | | Cyclohexane | 1 100 | 1.5 |

TABLE D-5

**Mass Spectrometer Analysis of Reaction Products from HDO of Tertiarybutylphenol**

| Run | Sample | Catalyst | Pressure psi | Reaction Products | Mass Spectrometer Counts | wt.% |
|---|---|---|---|---|---|---|
| 64 | 4 | Co-Mo-S (50g) | 1500 | Cyclohexane | 65 900 | 68.5 |
| | | | | Benzene | 21 200 | 22.0 |
| | | | | Dimethylcyclohexane | 4 200 | 4.4 |
| | | | | Dimethylbenzene | 2 000 | 2.1 |
| | | | | Methylcyclohexane | 1 700 | 1.8 |
| | | | | Toluene | 1 200 | 1.2 |
| 104 | 3 | Co-Mo-O (50g) | 1000 | Benzene | 107 800 | 59.4 |
| | | | | Cyclohexane | 58 100 | 32.0 |
| | | | | Dimethylbenzene | 10 800 | 6.0 |
| | | | | Toluene | 3 800 | 2.1 |
| | | | | Dimethylcyclohexane | 1 000 | 0.6 |
| 114 | 3 | Co-Mo-S (50g) | 1000 | Cyclohexane | 80 100 | 65.4 |
| | | | | Benzene | 35 600 | 29.1 |
| | | | | Dimethylbenzene | 4 100 | 3.3 |
| | | | | Toluene | 1 600 | 1.3 |
| | | | | Dimethylcyclohexane | 1 100 | 0.9 |
| 154 | 4 | Co-Mo-S (10g) | 1000 | Cyclohexane | 51 000 | 66.4 |
| | | | | Benzene | 20 500 | 26.7 |
| | | | | Dimethylbenzene | 3 300 | 4.3 |
| | | | | Toluene | 1 000 | 1.3 |
| | | | | Tetramethylbenzene | 1 000 | 1.3 |

# APPENDIX E

Gas Chromatograph Curves from

HDO of Phenolic Compounds Investigated

20-60-840127-2-4

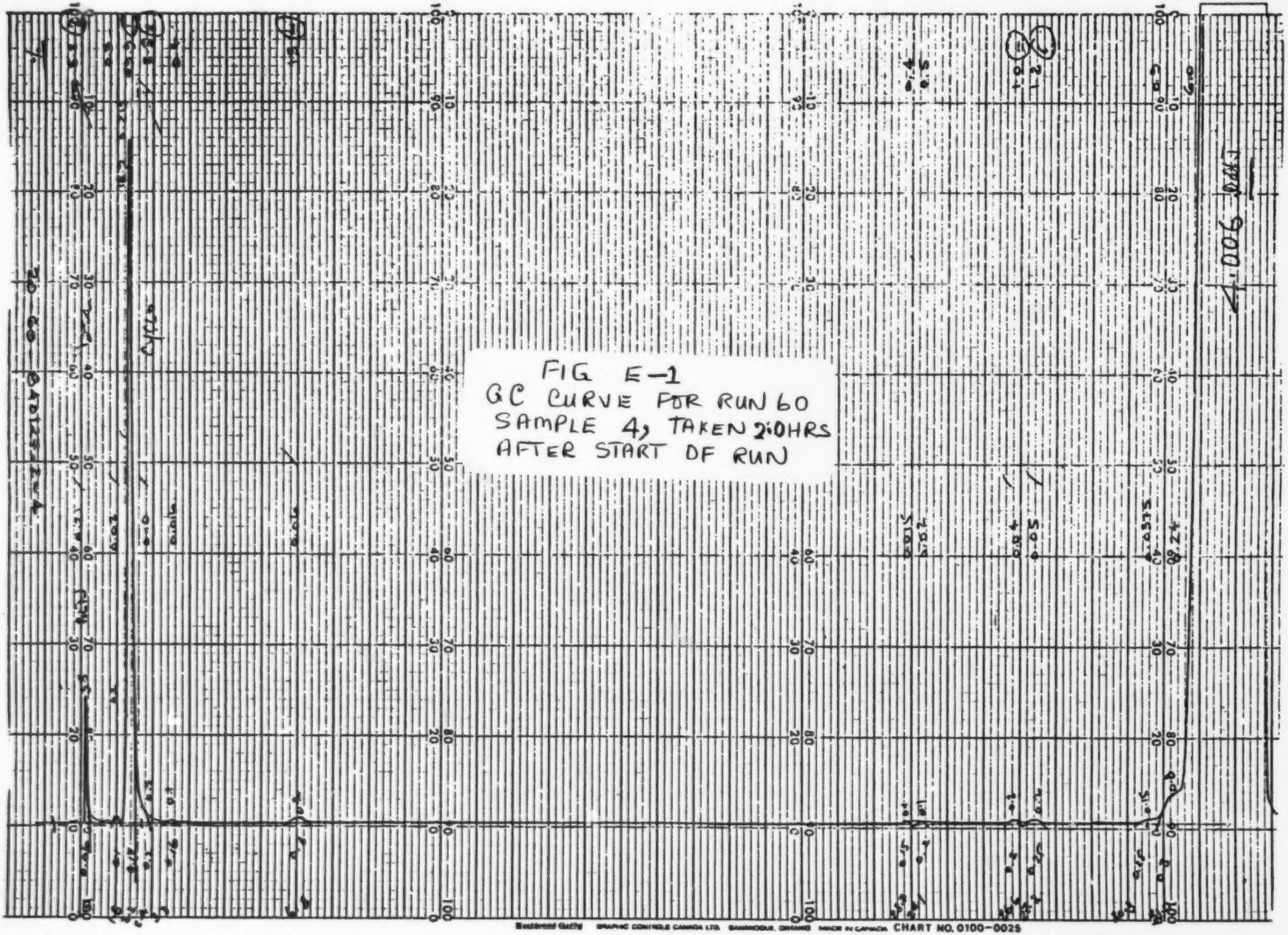


FIG E-1
GC CURVE FOR RUN 60
SAMPLE 4, TAKEN 2:0HRS
AFTER START OF RUN

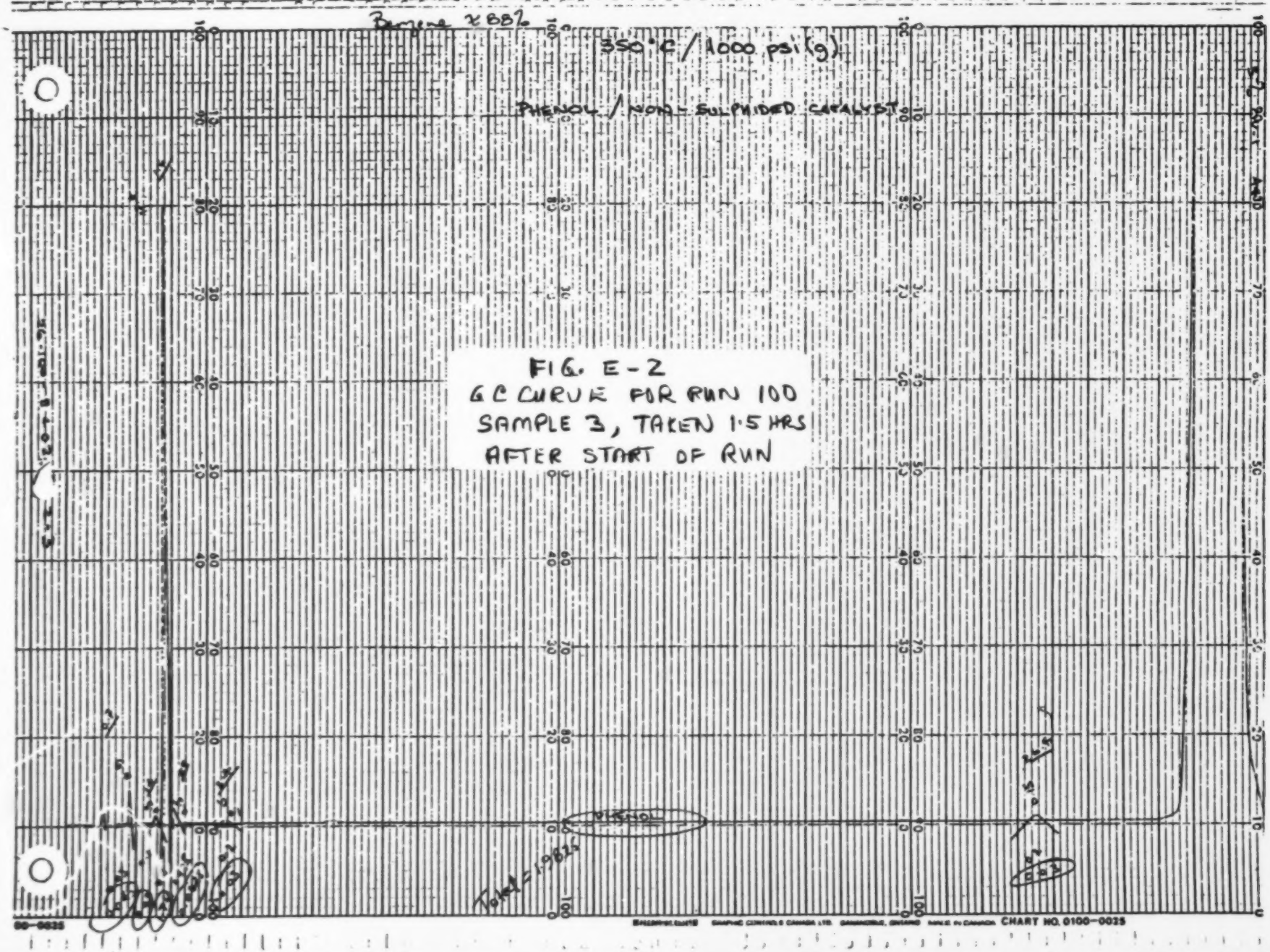



FIG. E-2
GC CURVE FOR RUN 100
SAMPLE 3, TAKEN 1.5 HRS
AFTER START OF RUN

36-150-840511-2-3

INST 1 METH 1 FILE 13

RUN 2 PHENOLS

SENSITIVITIES 50 4

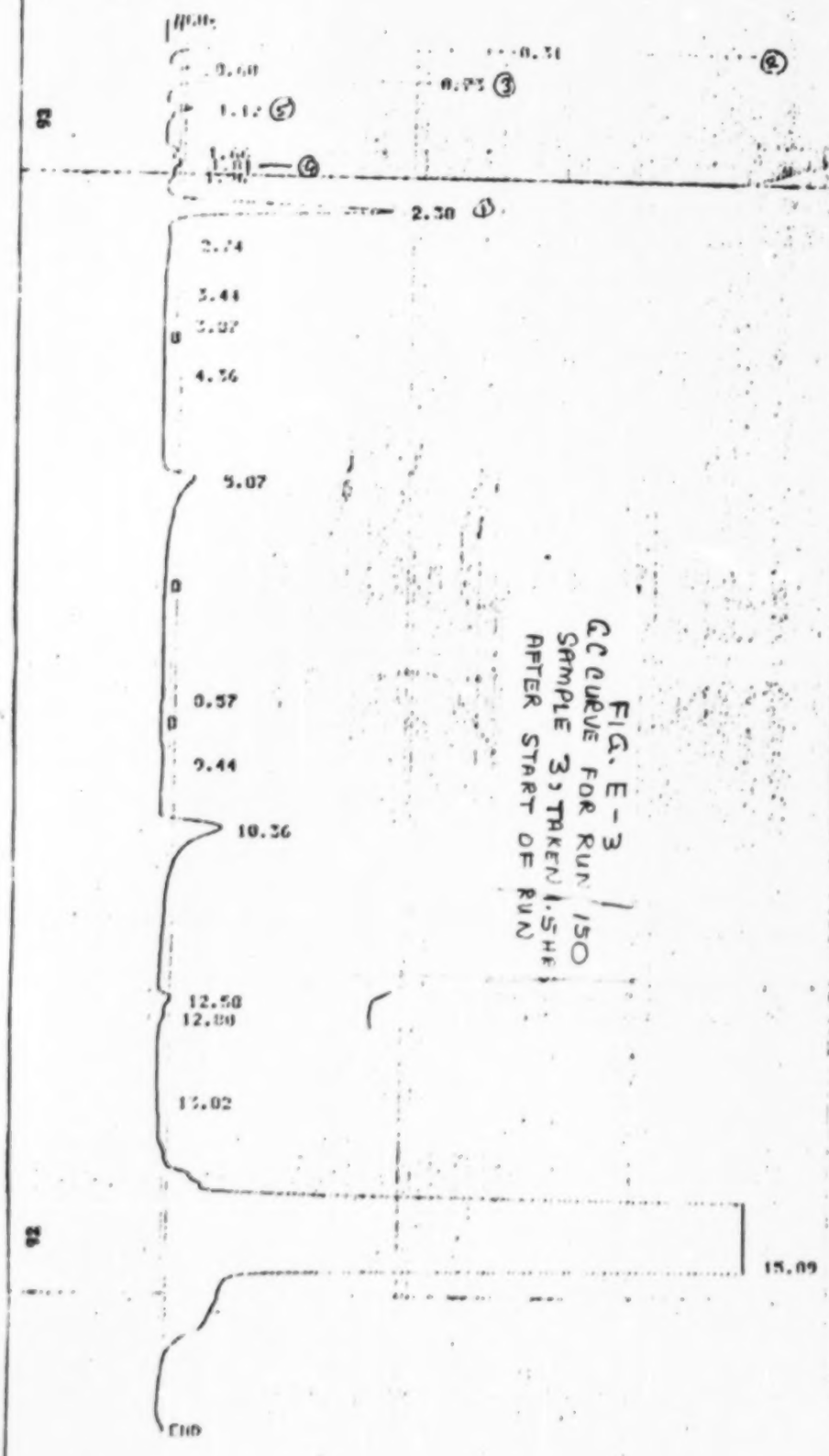



FIG. E-3
GC CURVE FOR RUN 150
SAMPLE 3; TAKEN 1.5 HR
AFTER START OF RUN

INST 1 METH 1 FILE 13

RUN 2 PHENOLS 9 : 35.4 6 / 0 / 84

36-150-3

SENSITIVITIES 50 4

| TIME | AREA | BC | RRT | RF | C | NAME |
|---|---|---|---|---|---|---|
| 0.31 | 1.9063 | T | 0.031 | 1.000 | 0.4575 | 16.68 2 |
| 0.60 | 0.1152 | T | 0.060 | 1.000 | 0.0220 | 1.01 |
| 0.83 | 1.6155 | T | 0.083 | 1.000 | 0.3822 | 14.14 3 |
| 1.12 | 0.1525 | B | 0.112 | 1.000 | 0.0352 | 2.03 5 |
| 1.66 | 0.1114 | T | 0.166 | 1.000 | 0.0262 | 0.97 |
| 1.81 | 0.1529 | T | 0.181 | 1.000 | 0.0352 | 1.56 4 |
| 2.30 | 0.1[illegible] | T | 0.230 | 1.000 | 0.0245 | 0.90 |
| 2.74 | 2.6862 | T | 0.274 | 1.000 | 0.6275 | 24.56 1 |
| 3.44 | 0.1523 | T | 0.344 | 1.000 | 0.0366 | 1.33 |
| 3.87 | 0.0152 | B | 0.344 | 1.000 | 0.0052 | 0.13 |
| 4.36 | 0.0822 | | 0.387 | 1.000 | 0.0087 | 0.02 |
| 4.56 | 0.0196 | B | 0.436 | 1.000 | 0.0052 | 0.17 |
| 5.07 | 1.2022 | | 0.507 | 1.000 | 0.2089 | 10.52 — unreacted |
| 0.57 | 0.0216 | | 0.057 | 1.000 | 0.0052 | 0.19 |
| 9.44 | 0.1120 | T | 0.944 | 1.000 | 0.0269 | 0.98 |
| 10.36 | 2.4942 | T | 1.036 | 1.000 | 0.5905 | 21.83 — Anthracene |
| 12.50 | 0.2106 | T | 1.250 | 1.000 | 0.0506 | 1.84 |
| 12.80 | 0.1120 | B | 1.280 | 1.000 | 0.0281 | 1.02 |
| 13.02 | 0.0116 | T | 1.302 | 1.000 | 0.0020 | 0.10 |

24-61-840209-2-4

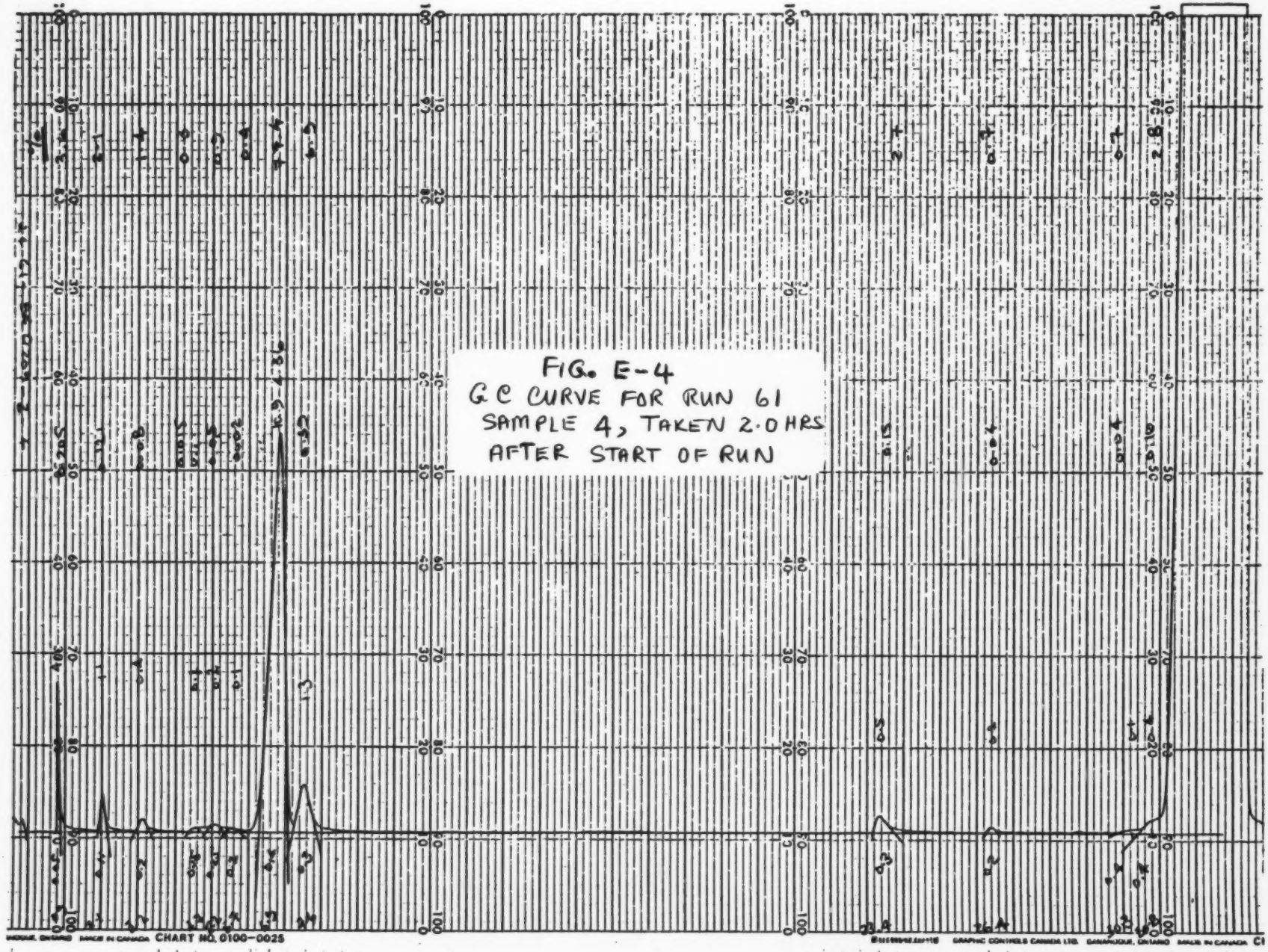


FIG. E-4
GC CURVE FOR RUN 61
SAMPLE 4, TAKEN 2.0 HRS
AFTER START OF RUN

28-101-840322-2-3

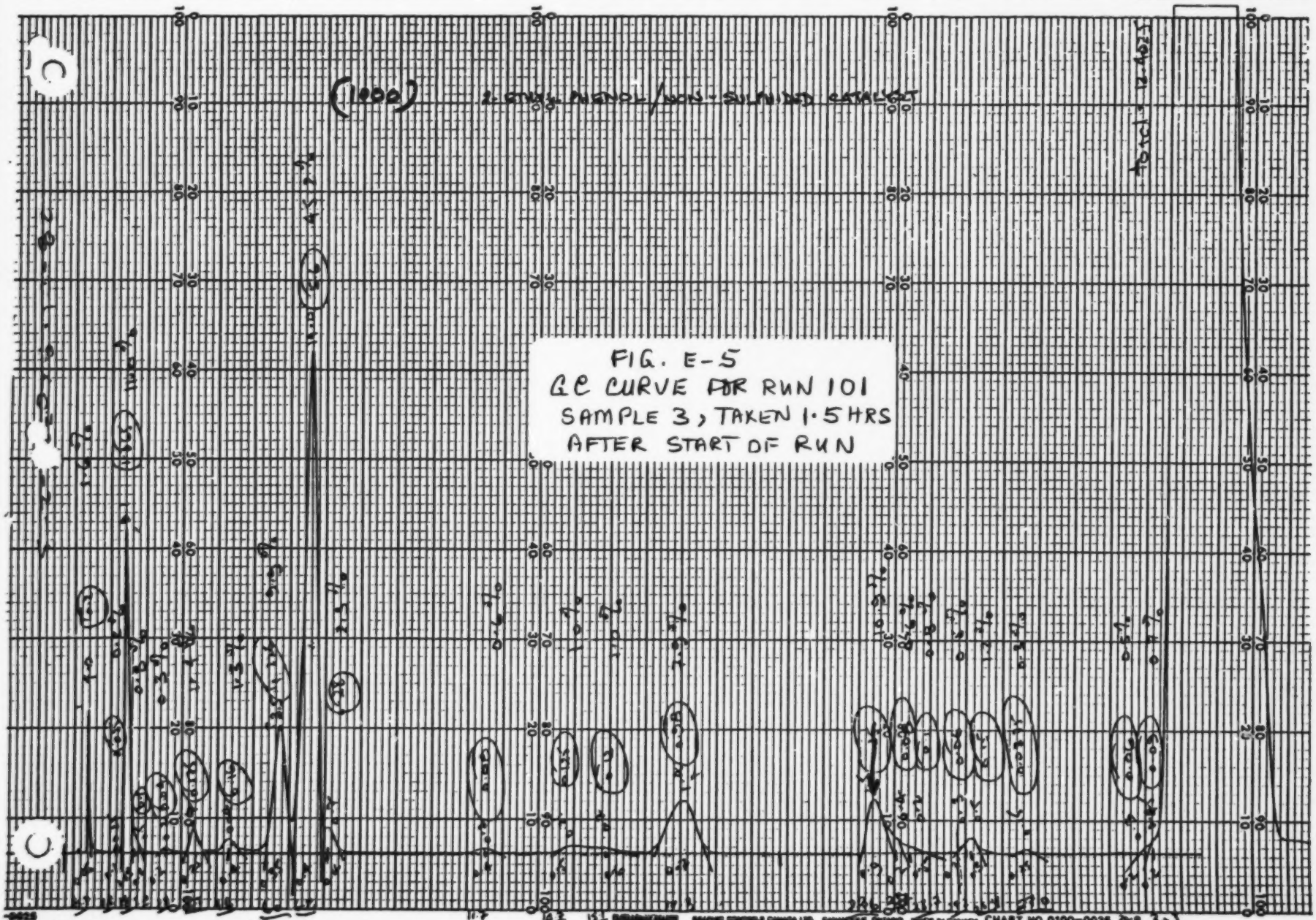



FIG. E-5
GC CURVE FOR RUN 101
SAMPLE 3, TAKEN 1.5 HRS
AFTER START OF RUN

37-151-840525-2-3

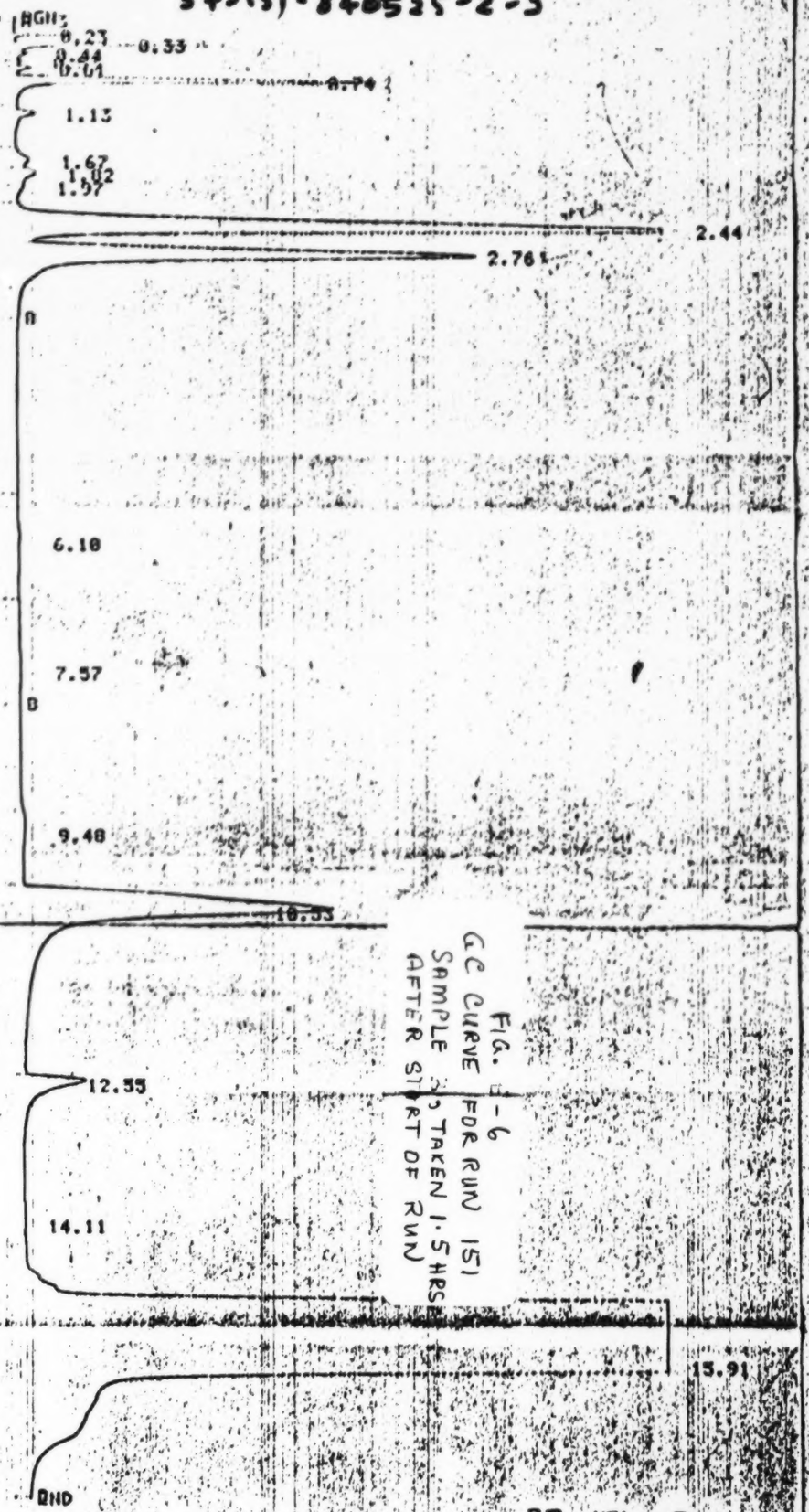



Fig. C-6
GC Curve for Run 151
Sample #5 Taken 1.5 Hrs
After Start of Run

37-151-3

INST 1 METH 1 FILE 12

RUN 3 PHENOLS 10 : 18.4 6 / 8 / 84

SENSITIVITIES 50 4

| TIME | AREA | DC | RRT | RF | C | NAME |
|---|---|---|---|---|---|---|
| 0.23 | 0.8976 | T | 0.023 | 1.000 | 0.0227 | 0.34 |
| 0.33 | 0.4407 | T | 0.033 | 1.000 | 0.1027 | 1.54 |
| 0.44 | 0.0524 | T | 0.044 | 1.000 | 0.0122 | 0.20 |
| 0.53 | 0.0259 | T | 0.053 | 1.000 | 0.0060 | 0.10 |
| 0.61 | 0.0683 | T | 0.061 | 1.000 | 0.0159 | 0.26 |
| 0.74 | 1.7099 | T | 0.074 | 1.000 | 0.3983 | 6.482 |
| 1.13 | 0.1685 | V | 0.113 | 1.000 | 0.0393 | 0.645 |
| 1.67 | 0.1326 | T | 0.167 | 1.000 | 0.0309 | 0.50 |
| 1.82 | 0.2171 | T | 0.182 | 1.000 | 0.0506 | 0.826 |
| 1.97 | 0.0081 | T | 0.197 | 1.000 | 0.0187 | 0.30 |
| 2.44 | 0.2694 | T | 0.244 | 1.000 | 1.9263 | 31.32 |
| 2.76 | 5.6320 | | 0.276 | 1.000 | 1.3120 | 21.33 |
| 6.10 | 0.0670 | V | 0.610 | 1.000 | 0.0156 | 0.25 |
| 7.57 | 0.0592 | | 0.757 | 1.000 | 0.0138 | 0.22 |
| 9.48 | 0.1224 | T | 0.948 | 1.000 | 0.0285 | 0.46 |
| 10.53 | 0.2259 | T | 1.053 | 1.000 | 0.0162 | 31.16 |
| 12.55 | 1.0085 | V | 1.255 | 1.000 | 0.1349 | 3.82 |
| 14.11 | 0.0220 | V | 1.411 | 1.000 | 0.1051 | 0.08 |
| 15.91 | 402.8825 | | 1.591 | 1.000 | 13.0502 | |

R1-62-BAD131-2-4

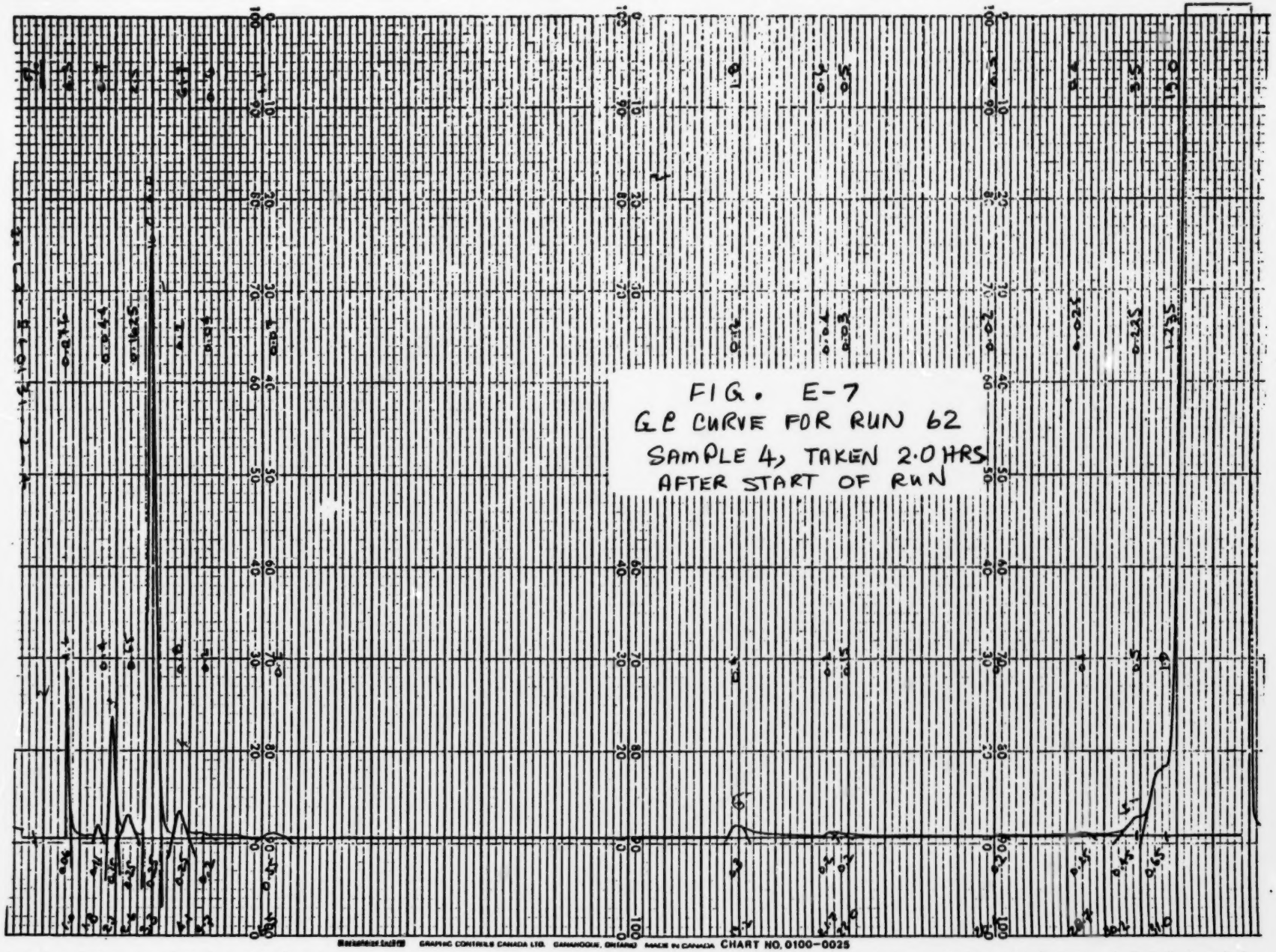
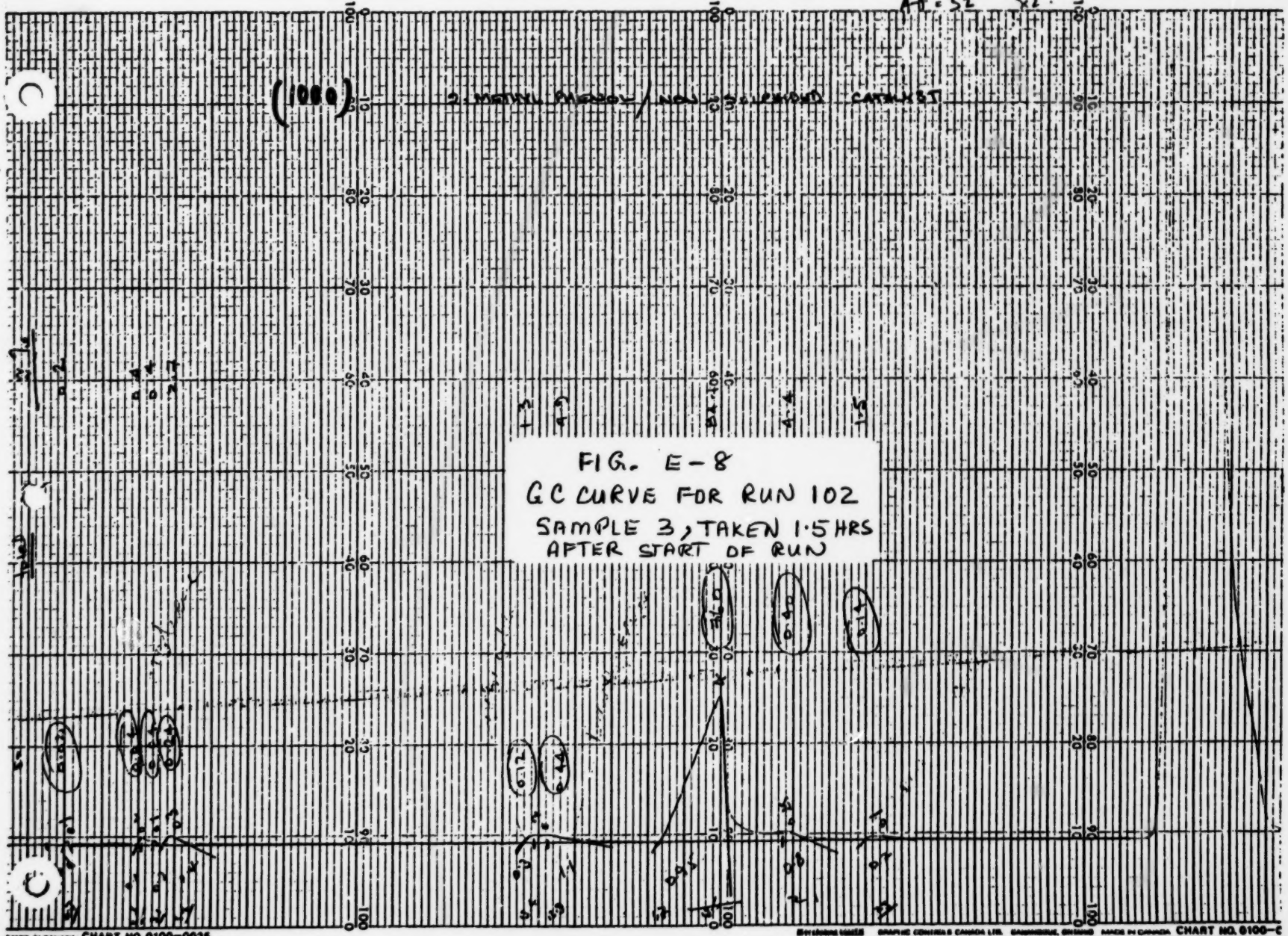


FIG. E-7
GC CURVE FOR RUN 62
SAMPLE 4, TAKEN 2.0 HRS
AFTER START OF RUN

GRAPHIC CONTROLS CANADA LTD. CANANOQUE, ONTARIO MADE IN CANADA CHART NO. 0100-0025

30-102, 840309-2-3



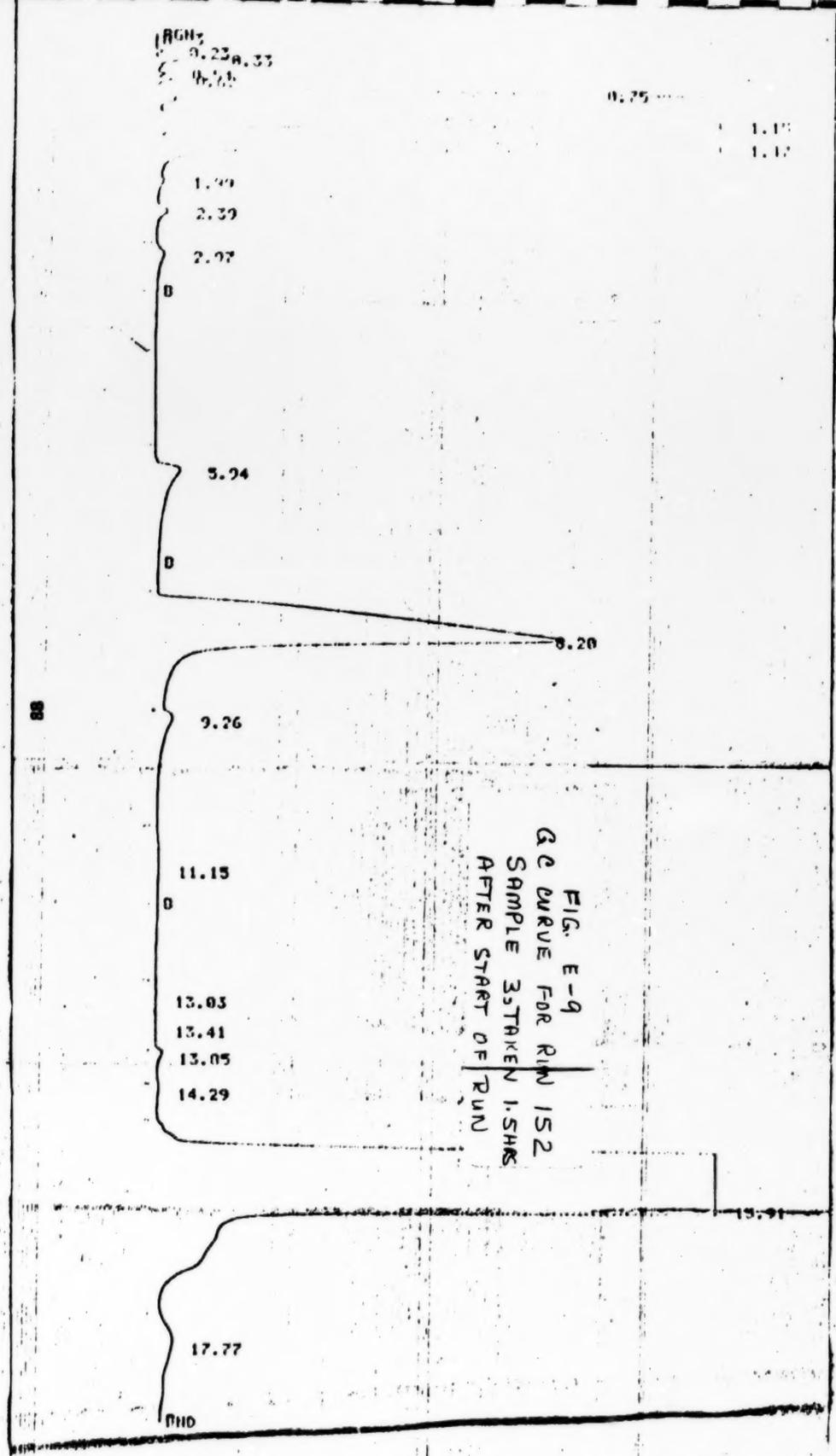



FIG. E-9
GC CURVE FOR RUN 152
SAMPLE 3 TAKEN 1.5HRS
AFTER START OF RUN

38-152-3

INST 1 METH 1 FILE 11

RUN 4 PHENOLS 10 : 55.5 6 / 8 / 84

SENSITIVITIES 10 4

| TIME | AREA | BC | RRT | RF | C | UNUN |
|---|---|---|---|---|---|---|
| 0.23 | 0.0243 | T | 0.023 | 1.000 | 0.0055 | 0.06 |
| 0.33 | 0.2930 | T | 0.033 | 1.000 | 0.0669 | 0.70 |
| 0.54 | 0.0381 | T | 0.054 | 1.000 | 0.0087 | 0.09 |
| 0.62 | 0.0720 | T | 0.062 | 1.000 | 0.0164 | 0.16 |
| 0.75 | 3.1630 | T | 0.075 | 1.000 | 0.7218 | 3.26 |
| 1.15 | 9.9272 | T | 0.115 | 1.000 | 2.2762 | 10.04 |
| 1.47 | 0.1001 | T | 0.147 | 1.000 | 2.0961 | 0.28 |
| 1.99 | 0.1254 | T | 0.199 | 1.000 | 0.0286 | 0.22 |
| 2.39 | 0.1665 | V | 0.239 | 1.000 | 0.0380 | 0.26 |
| 2.97 | 0.1700 | | 0.297 | 1.000 | 0.0400 | 0.27 |
| 5.94 | 0.9957 | | 0.594 | 1.000 | 0.2272 | 1.09 |
| 8.20 | 16.5952 | T | 0.820 | 1.000 | 3.7859 | 16.69 |
| 9.26 | 0.6398 | V | 0.926 | 1.000 | 0.1459 | 0.93 |
| 11.15 | 0.0582 | | 1.115 | 1.000 | 0.0133 | 0.15 |
| 13.03 | 0.0247 | V | 1.303 | 1.000 | 0.0057 | 0.12 |
| 13.41 | 0.0024 | V | 1.341 | 1.000 | 0.0022 | 0.10 |
| 13.85 | 0.1194 | T | 1.385 | 1.000 | 0.0272 | 0.21 |
| 14.29 | 0.0594 | V | 1.429 | 1.000 | 0.0136 | 0.15 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | |
| 17.77 | 0.7917 | | 1.777 | 1.000 | 0.1806 | |

39.77 unreacted

22-63-840203-2-4

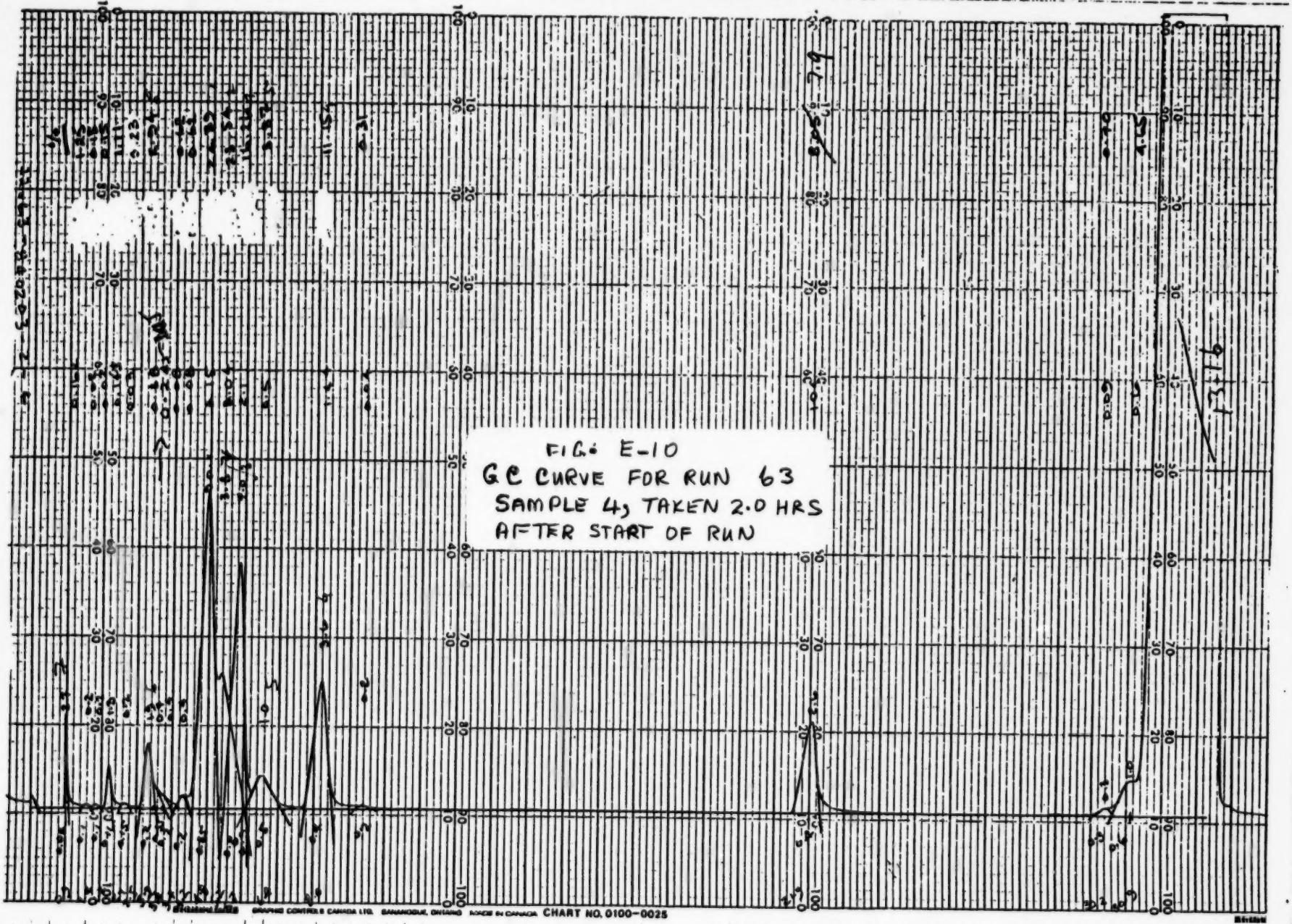


FIG. E-10
GC CURVE FOR RUN 63
SAMPLE 4, TAKEN 2.0 HRS
AFTER START OF RUN

32-103-840314-2-3

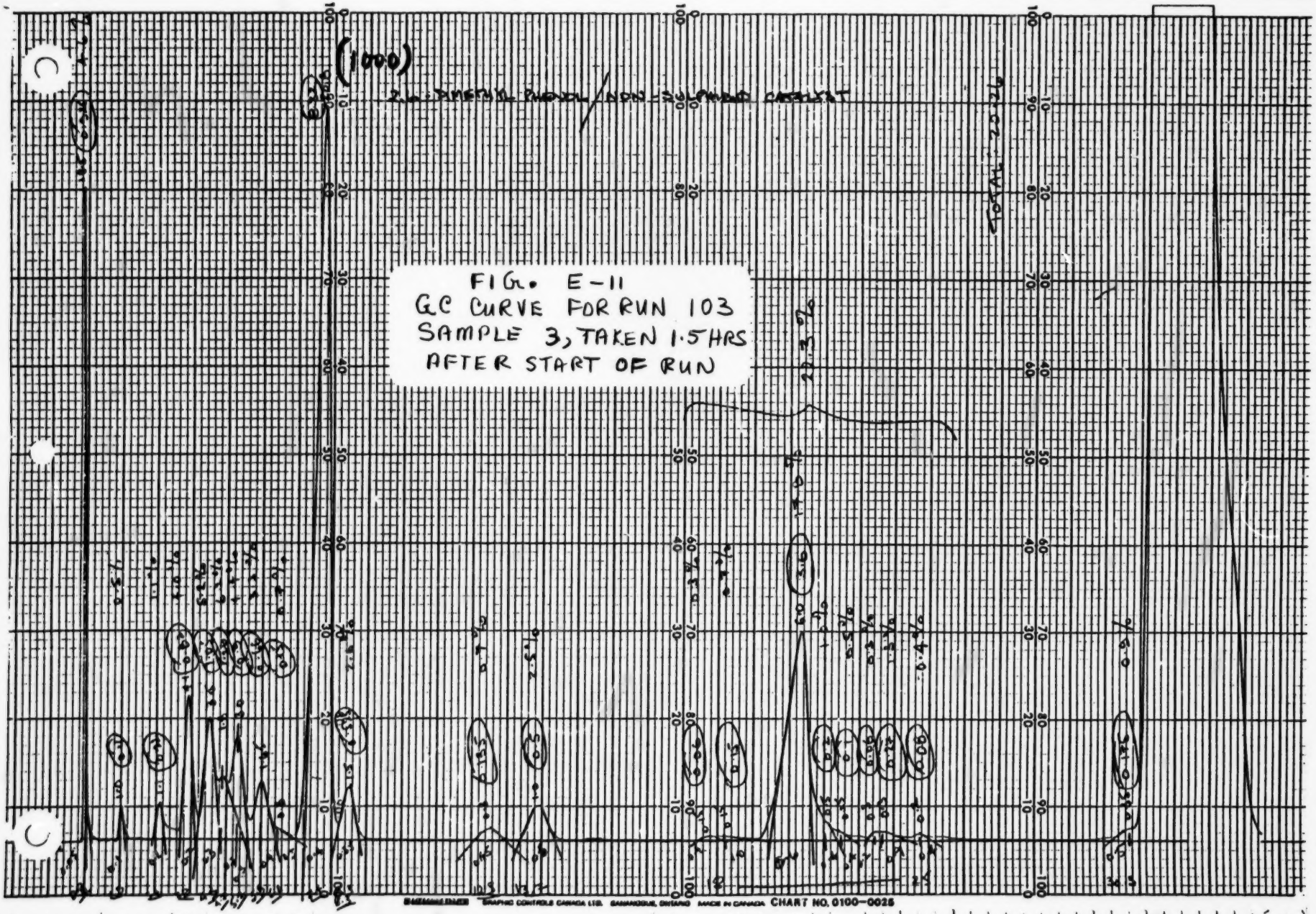



FIG. E-11
GC CURVE FOR RUN 103
SAMPLE 3, TAKEN 1.5 HRS
AFTER START OF RUN

33-113-8401313-2-3

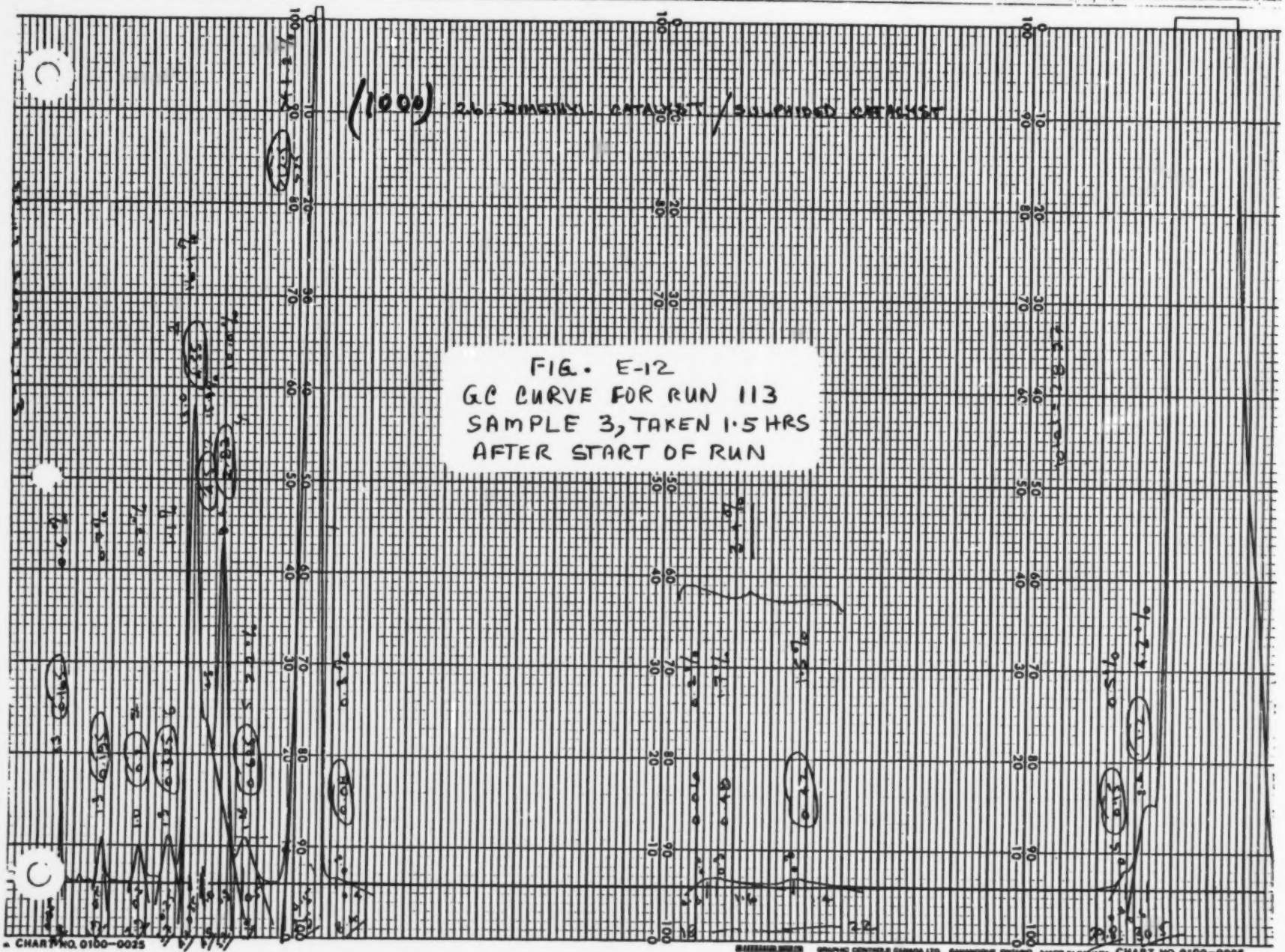



FIG. E-12
GC CURVE FOR RUN 113
SAMPLE 3, TAKEN 1.5 HRS
AFTER START OF RUN

CHART NO. 0100-0025

GRAPHIC CONTROLS CANADA LTD. BRANTFORD, ONTARIO MADE IN CANADA CHART NO. 0100-0025

32-133-840517-2-3

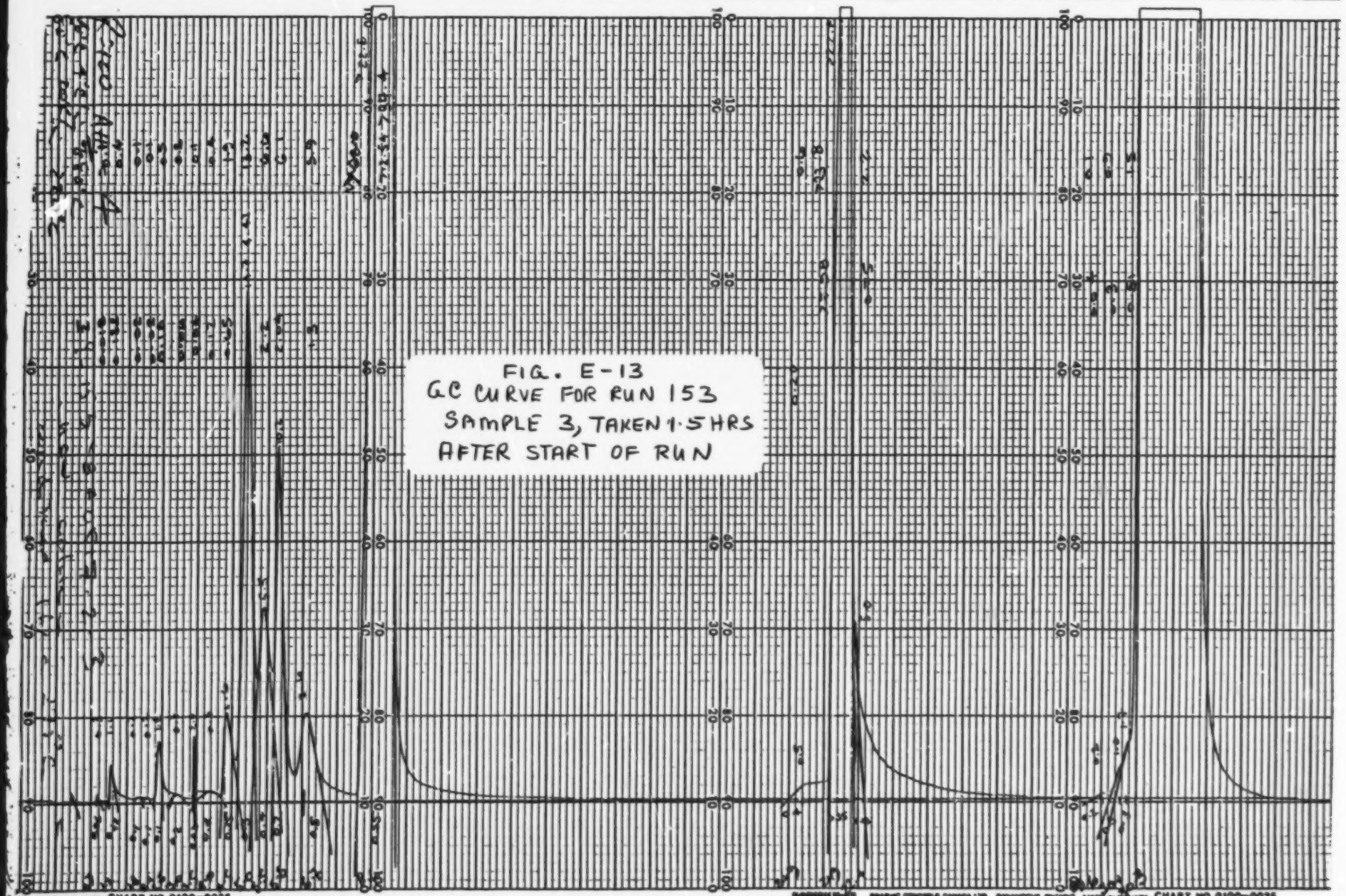


FIG. E-13
GC CURVE FOR RUN 153
SAMPLE 3, TAKEN 1.5 HRS
AFTER START OF RUN

23-64-840207-2-4

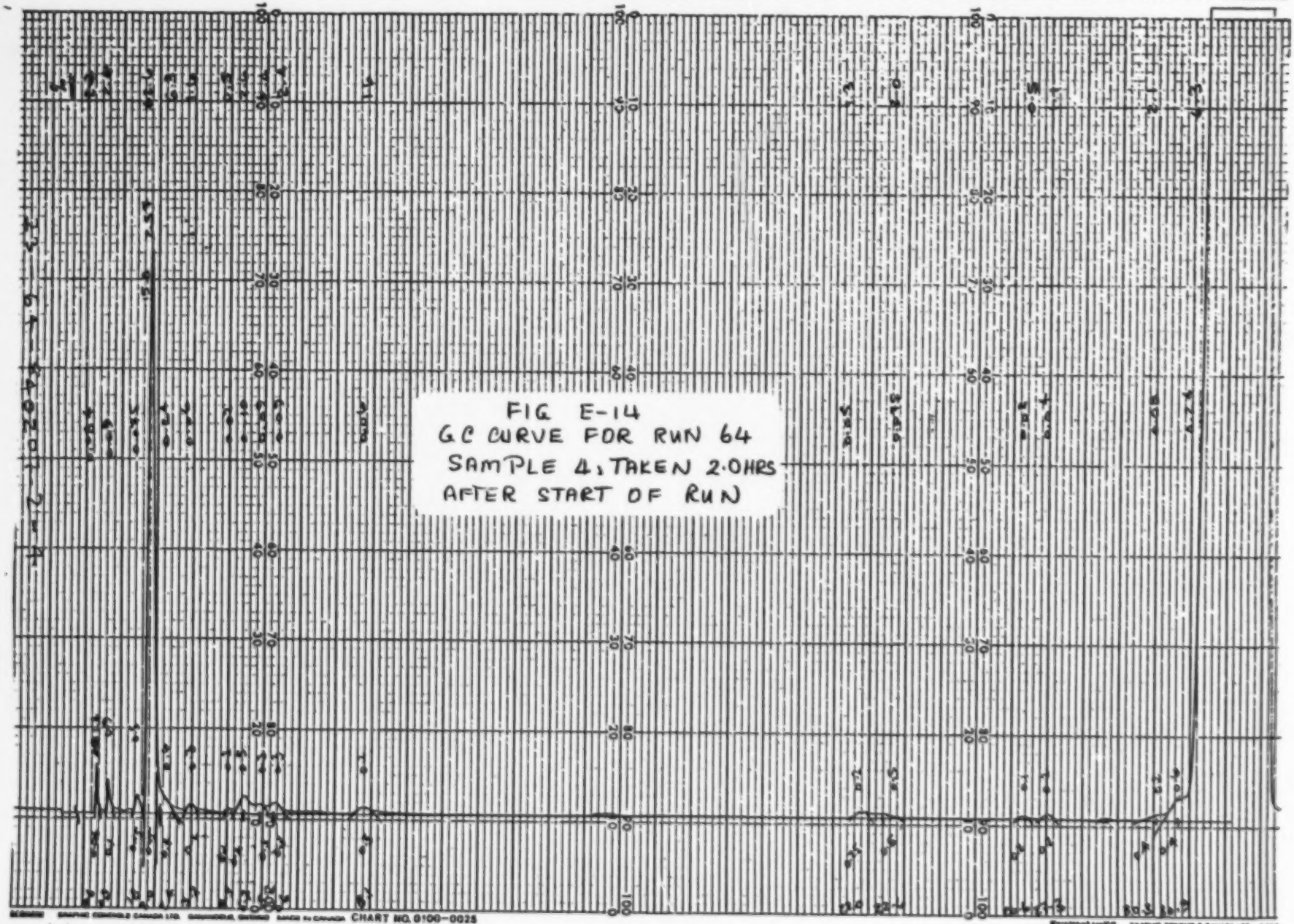


FIG E-14
GC CURVE FOR RUN 64
SAMPLE 4, TAKEN 2.0HRS
AFTER START OF RUN

34-104-840319-2-3

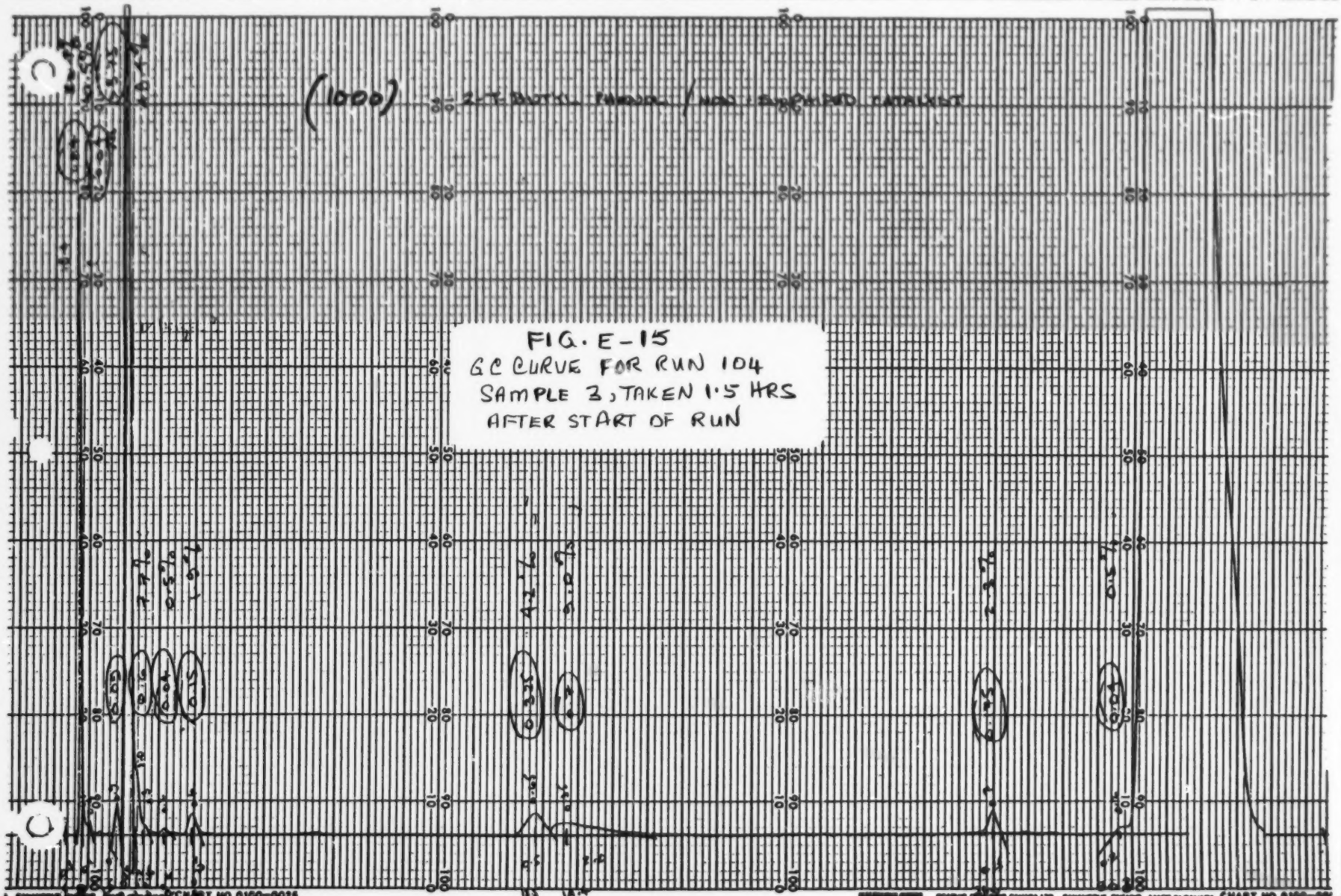


FIG. E-15
GC CURVE FOR RUN 104
SAMPLE 3, TAKEN 1.5 HRS
AFTER START OF RUN

35-114-84034-2-3

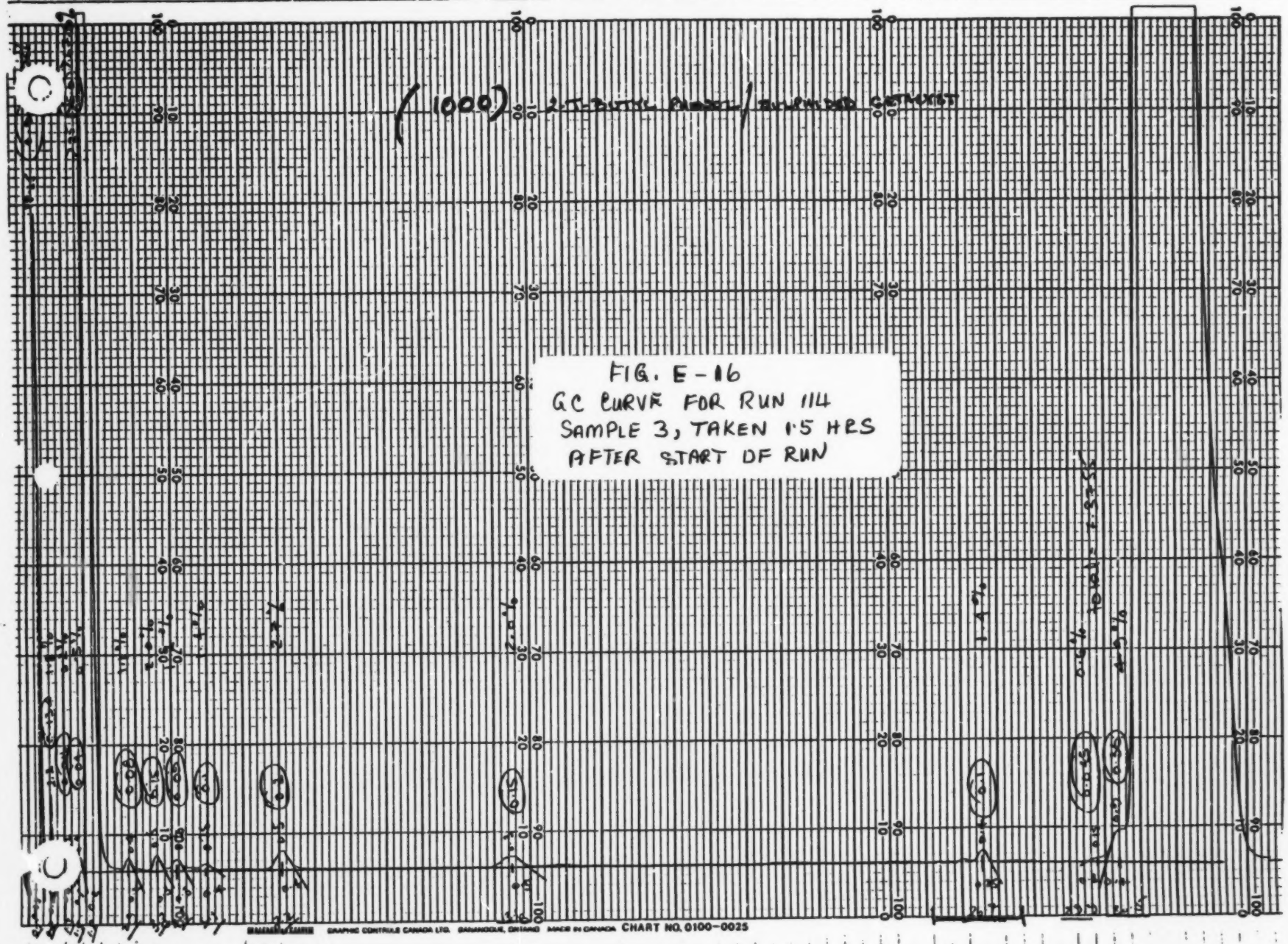
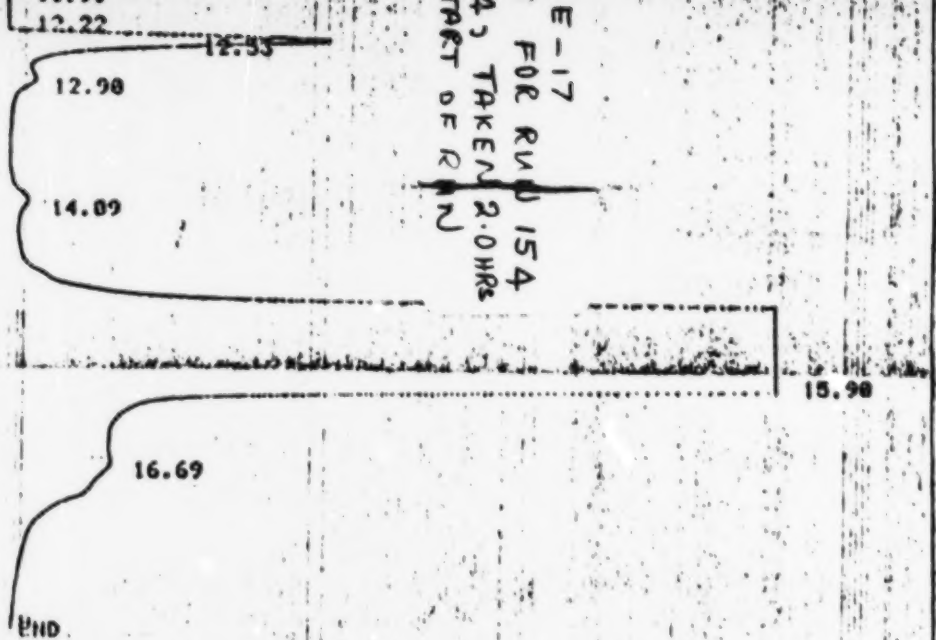



FIG. E-16
GC CURVE FOR RUN 114
SAMPLE 3, TAKEN 1.5 HRS
AFTER START OF RUN

40-154-840523-2-4




FIG. E-17
GC CURVE FOR
SAMPLE 4, TA
AFTER START O




40-154-4

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RUN 14 PHENOLS 2 : 38.6 6 / 11 / 84

SENSITIVITIES 50 4

| TIME | AREA | BC | RRT | RF | C | NAME |
|---|---|---|---|---|---|---|
| 0.23 | 0.8156 | T | 0.023 | 1.000 | 0.1056 | 3.15 |
| 0.33 | 0.6443 | T | 0.033 | 1.000 | 0.1466 | 2.49 |
| 0.53 | 0.0320 | T | 0.053 | 1.000 | 0.0075 | 0.13 |
| 0.61 | 0.1587 | T | 0.061 | 1.000 | 0.0361 | 0.61 |
| 0.75 | 13.2622 | T | 0.075 | 1.000 | 3.9203 | 66.74 |
| 1.13 | 0.1732 | T | 0.113 | 1.000 | 0.0394 | 0.67 |
| 1.66 | 0.1978 | T | 0.166 | 1.000 | 0.0458 | 0.76 |
| 1.90 | 0.0916 | T | 0.190 | 1.000 | 0.0208 | 0.35 |
| 2.40 | 0.0553 | | 0.240 | 1.000 | 0.0126 | 0.21 |
| 3.83 | 0.8668 | | 0.383 | 1.000 | 0.0158 | 0.26 |
| 4.08 | 0.0898 | U | 0.408 | 1.000 | 0.0011 | 0.02 |
| 5.20 | 0.1985 | T | 0.578 | 1.000 | 0.0452 | 0.77 |
| 5.81 | 2.2006 | | 0.581 | 1.000 | 0.5026 | 8.54 |
| 9.61 | 0.0455 | | 0.961 | 1.000 | 0.0104 | 0.18 |
| 11.91 | 0.0003 | T | 1.191 | 1.000 | 0.0022 | 0.04 |
| 12.22 | 0.0161 | T | 1.222 | 1.000 | 0.0037 | 0.04 |
| 12.98 | 0.0494 | T | 1.298 | 1.000 | 0.6384 | 10.86 |
| 14.09 | 0.4203 | T | 1.409 | 1.000 | 0.1070 | 1.82 |
| 15.98 | 0.4209 | T | 1.598 | 1.000 | 0.0976 | 1.66 |
| 16.69 | 4.8446 | | 1.669 | 1.000 | 0.9284 | |

## APPENDIX F

List of Components of the Continuous-flow, High-pressure Reactor - Descriptions & Manufacturers

TABLE F-1

LIST OF COMPONENTS OF CONTINUOUS FLOW HIGH-PRESSURE REACTION SYSTEM

| Item No | Qty | Description | Manufacturer |
|---|---|---|---|
| 1 | 1 | 193 ml High Pressure Double Ended Reactor, 1" inside dia., 15" inside LG 316 Stainless Steel, 11000 psi max. W.P. | AE |
| 2 | 1 | 2-Litre Capacity Receiver, 3" inside dia., 316 Stainless Steel, 11000 psi max. W.P. | SHP Enterprises |
| 3 | 1 | 1-Litre Capacity Receiver, 3" inside dia., 316 Stainless Steel, 11000 psi max. W.P. | SHP Enterprises |
| 4 | 1 | Model LS 30 Pulsafeeder Diaphragm Metering Pump, 3000 psig, max. W.P. 0.15 gpm capacity. | Pulsafeeder Products |
| | | Drive Motor 1/12 HP, 115 VAC, 60 cy 1-phase, 1725 rpm. | G.E. |
| 5 | 1 | CLFX 9900 5/10 Line Filter | AE |
| 6 | 1 | SG 3810-30 Pressure Reducing Valve | Linde |
| 7 | 1 | 30 VRMM 4812 TG Micro Metering Valve | AE |
| 8 | 1 | Model 100H - 11 - 16454 Standard Century Flowmeter | Century |
| 9 | 14 | Series SC Medium Press. Valve | AE |
| 10 | 2 | CXO 4400 Stainless Steel Check Valve | AE |
| 11 | 2 | CSX 4600 3/16F Safety Disc Assembly | AE |
| 12 | 1 | TSK 4-16 Thermocouple, 16" dia. | AE |
| 13 | 1 | Series 2961 3-Zone Heating Furnace, 3100 watts, 9-amps per zone, 110 volt AC | Applied Test System Inc. |

| Item No | Qty | Description | Manufacturer |
|---|---|---|---|
| 14 | 1 | C-1271 Temperature Controller System with 3-Zone Controllers, Temperature Regulated by Proportional Controlling Device, 120 volt AC, 45-Amps | Elkon Elec. |
| 15 | 1 | Digimite digital Temperature Indicator | Digimite |
| 16 | 3 | 11463 - 50C 120 Volt AC, 620 watts 6' long, 1" wide Flexible Electric Heating Tape, controlled with one only MC 221, 115 Volt, 1500 Watt Temperature Regulator | Thermolyne Corp. |

POOR
QUALITY
ORIGINAL